EVALUATING THE EFFECT OF ALTERNATIVE NEUTRALISING AGENT AND SEEDING ON THE ZINC RECOVERY THROUGH THE ZINCOR IRON REMOVAL CIRCUIT

by

Diane Taggart

Submitted in partial fulfilment of the requirements of the degree

Master of Science in Hydrometallurgy

in the
Department of Chemical Engineering
University of Cape Town
Cape Town, South Africa

February 2016

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ABSTRACT:

Zincor's average zinc recovery was 90.29 % (for the period of 1 January 2009 to 30 September 2011), which was well below the industry standard of 96 %. Due to limitations in Zincor's iron removal technology, the maximum achievable recovery was 94 %. The zinc loss through the iron residue was the second biggest contributor to the overall zinc losses, so that there was much room for improvement.

The calcine used for neutralisation in the Iron Removal Stage contained a portion of insoluble zinc ferrite. The insoluble zinc loss through the iron residue was associated with the presence of the insoluble zinc ferrite, as well as the phenomenon of coating of unleached neutralising agent by iron precipitate. The soluble zinc loss was a function of the dewatering characteristics of the precipitate.

The work included the evaluation of alternative neutralising agents to supplement or replace calcine, as well as the implementation of a seed recycle. A review of literature found that the use of an alternative neutralising agent that contained little or no zinc could potentially reduce the insoluble portion of the zinc loss. Secondly, the presence of seed could potentially reduce both the soluble and insoluble zinc losses by promoting agglomeration growth and providing additional surface area for precipitation to occur (thereby reducing coating of zinc-rich neutralising agents).

The laboratory work evaluated a number of alternative neutralising agents, but focused on the use of DRC oxide and limestone for neutralisation. These were evaluated separately and in combination, with and without a seed recycle.

The use of limestone for neutralisation achieved a zinc recovery of 95.10 %. While the insoluble zinc loss decreased, there was a significant increase in the soluble zinc loss to 3.66 %. This was attributed to the formation of a large volume of very fine precipitate with poor settling and filtration characteristics. This was confirmed by the PSD, XRD and SEM analyses.

The use of DRC oxide gave a recovery of 95.96 %. At 2.91 % the insoluble zinc loss made up the biggest portion of the total loss, and was attributed to coating of the zinc-rich neutralising agent with iron precipitate. Since a low volume of residue (accompanied by a high wash ratio) with good settling and filtration characteristics was generated, the soluble zinc loss was low. The addition of a seed recycle to this scenario resulted in an increase in both the soluble and insoluble zinc losses. The increase in soluble loss was attributed to an increase in the residue volume and a low wash ratio. It was believed

that the increase in the insoluble zinc loss could be attributed to the 33.33 % decrease in residence time as a result of the 50 % volume seed recycle.

The combination of DRC oxide and limestone for neutralisation showed the best performance with a zinc recovery of 96.20 %. This scenario achieved very low insoluble zinc losses, which was attributed to the higher reactivity of the combination of these neutralising agents compared to calcine. The high soluble zinc loss was attributed to poor settling and filtration characteristics of the precipitate, as well as a high residue volume and low wash ratio. The addition of a seed recycle to this scenario resulted in an increase in the insoluble zinc loss, which was attributed to a decrease in the residence time as a result of the seed recycle.

A plant trial evaluated the implementation of a seed recycle. The seed recycle rate was increased gradually over a 4-week period. With the implementation of a seed recycle of 2 m^3/hr, there was an initial decrease in the soluble losses from approximately 1.4 to 0.8 %. The improvement was credited to the presence of seed, which promotes agglomeration growth and results in a coarser and denser precipitate with good dewatering characteristics. As the seed recycle was increased further to 4 and 6 m^3/hr (which equates to approximately a 50 % volume recycle), the soluble loss increased to between 1.4 and 1.6 %. This result was attributed to an increase in the residue volume and the accompanying low wash ratio, particle crowding, particle breakage and attrition. The presence of seed provided additional surface area for precipitation to occur so that there was less coating of unleached neutralising agent over the 4-week period. The result was a decrease in the insoluble zinc losses from approximately 11 to 6 %.

In conclusion, the use of an alternative neutralising agent that contained no zinc (limestone in this scenario) decreased the insoluble zinc loss. Unfortunately this improvement was negated by the significant increase in the soluble zinc loss, which was attributed to the generation of a large volume of very fine precipitate with poor dewatering characteristics. Managing seed, wash ratio and residence time could potentially address this issue. The presence of seed promoted agglomeration growth, reducing the soluble zinc loss. Seed also provided additional surface area for precipitation to occur, minimising the instances of coating of fresh neutralising agent by iron precipitate, thereby reducing the insoluble zinc loss. However, the benefit of seed was only realised when the implementation of a seed recycle was not done at the expense of wash ratio or residence time.

ACKNOWLEDGEMENTS:

'And whatever you do, whether in word or deed, do it all in the name of the Lord Jesus, giving thanks to God the Father through him.' (Colossians 3:17)

First and foremost I would like to thank my Heavenly Father for His constant encouragement and guidance. Thank you for giving me strength when I wanted to give up.

'I can do all things through Christ who strengthens me.' (Philippians 4:13)

This project could not have been completed without the support of a number of my supervisors and colleagues at Zincor. Thank you to Jacolien Wyethe and Rasai Ntsoelengoe for allowing me much time away from the office and providing the financial assistance to complete the experimental work. Thanks to Frikkie de Bruin, Gideon Kriel and the RTP personnel for assisting me with sampling. Loads of gratitude go to Glynnis and the laboratory personnel who analysed countless samples (on top of their normal workload!) without complaint.

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My sincere thanks goes to Dr Jochen Petersen, my supervisor at the university. Thank you for being tremendously patient with me and for countless hours spent mentoring and editing.

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LIST OF ABBREVIATIONS:

- BZS: Basic Zinc Sulphate
- DRC: Democratic Republic of Congo
- ETP: Effluent Treatment Plant
- EZ: Electrolytic Zinc
- FS: Final Solution
- HAL: Hot Acid Leach
- HIS: Hot Iron Solution
- ICP: Inductively Coupled Plasma
- IS: Impure Solution
- JSE: Johannesburg Stock Exchange
- LIMS: Laboratory Information Management System
- RLE: Roast Leach Electrowin
- PS: Purified Solution
- PSD: Particle Size Distribution
- SCADA: Supervisory Control and Data Acquisition
- SEM-EDX: Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis
- SG: Specific Gravity
- SHAL: Super Hot Acid Leach
- WAB: Weak Acid Bleed
- WAL: Weak Acid Leach
- XRD: X-Ray Diffraction

1. INTRODUCTION:

Zincor was a zinc metal and sulphuric acid producer situated just outside of Springs in the Gauteng Province of South Africa. The zinc metal was sold mostly for use in galvanising operations and the sulphuric acid product was sold into the agricultural industry to manufacture fertiliser.

Zincor's recovery had always been below the industry standard of 96 %. There were a number of reasons for this, some of which included the age of the facility and the equipment, the complexity of the operation, as well as the chosen technology, particularly in the Iron Removal Stage. Primary zinc losses were through the residues from the Residue Treatment Plant, which accounted for almost half of the total losses. Any focus for recovery improvement was, therefore, on the Iron Removal Stage in the Residue Treatment Plant.

1.1. HISTORY OF ZINCOR:

Prior to 1969, all zinc used in South Africa had to be imported [Zincor R&D, undated]. In the late 1960's Gold Fields of South Africa Limited converted their mothballed Vogelstruisbult G.M.C uranium recovery plant into an electrolytic zinc refinery. The first sulphuric acid was produced in December 1968, with the first zinc ingot being cast four months later. In 1999 Goldfields sold their majority share-holding to Iscor. In 2001 Iscor Limited unbundled their steel, coal, zinc, mineral sands and iron ore assets. The mining assets were listed as Kumba Resources on the JSE in November of that same year. In November 2006 Kumba Resources unbundled their iron ore assets and relisted as Kumba Iron Ore. The remaining coal, base metals and mineral sands operations, combined with four coal assets owned by Eyesizwe Coal, became known as Exxaro Resources. Zincor was owned by Exxaro Base Metals until its closure in December 2011.

During the four decades that Zincor was operational, it expanded to a zinc capacity of approximately 100 000 tpa and a sulphuric acid capacity of approximately 200 000 tpa. Until its closure, Zincor was the only zinc producer in South Africa and maintained its position as one of the country's major sulphuric acid producers.

1.2. PROCESS DESCRIPTION:

Zinc smelting on an industrial scale is believed to have originated in China in the seventh century AD. India was producing zinc by 1380 and Europe was importing zinc from Asia by the seventeenth century. The first zinc smelter for the treatment of zinc oxide was erected in Bristol, England in 1743. By the early nineteenth century zinc smelting was well established in Germany and Belgium and by 1917 the electrolytic extraction of zinc from zinc sulphate solutions had been developed [Van Niekerk and Begley, 1991; Zincor R&D, undated].

1.2.1. OVERALL ZINCOR PROCESS DESCRIPTION:

Zincor operated a typical roast-leach-electrowin (RLE) circuit. This type of process accounts for 75 to 80 % of the annual primary zinc production in the world. The refinery fed up to 220 000 tpa of zinc sulphide concentrate. The major portion of the raw material was sourced in Southern Africa from the Rosh Pinah and Black Mountain mines. Between 20 000 to 40 000 tpa of material was imported to make up the deficit and to 'sweeten', or improve the grade, of the feed material.

A simplified flow sheet of the Zincor process can be seen in *Figure 1*. The zinc sulphide concentrates were roasted in fluidized bed roasters to produce a zinc oxide, known as calcine. The SO_2 off-gas from the roasting process was scrubbed to remove any residual solids and impurities before being converted to concentrated sulphuric acid (H_2SO_4) in the Acid Plant. The strength of the acid produced exceeded 98 %. A portion of the sulphuric acid was used for leaching in the Residue Treatment Plant, while the majority was sold. The impurities scrubbed from the SO_2 gas stream exited the plant in the weak acid bleed (WAB) via the Effluent Treatment Plant.

The calcine contained an average of 57.71 % Zn and 6.33 % Fe (for the period of 1 January 2009 to 30 September 2011) and was sent to the Neutral Leach Plant, where spent electrolyte from the electrowinning circuit was used for leaching. This was an atmospheric leach with a final pH of up to 4.4 and a temperature of approximately 60 ^{o}C. The leaching reaction was exothermic and required no heating. Between 80 and 90 % of the zinc contained in the calcine, along with impurities, were leached during this stage. The increase in the pH profile across the four leach tanks resulted in some of the dissolved zinc re-precipitating as Basic Zinc Sulphate. The leaching operation was followed by a thickening step. The thickener overflow solution, containing the dissolved zinc and some impurities, was known as Impure Solution. This solution was sent to the Purification Plant for the removal of the impurities through cementation with zinc dust. The thickener underflow, or Neutral Leach residue,

contained as much as 19.61 % Zn. This residue was sent to the Residue Treatment Plant, where more aggressive leaching conditions aided in the recovery of the residual zinc and the re-precipitated Basic Zinc Sulphates.

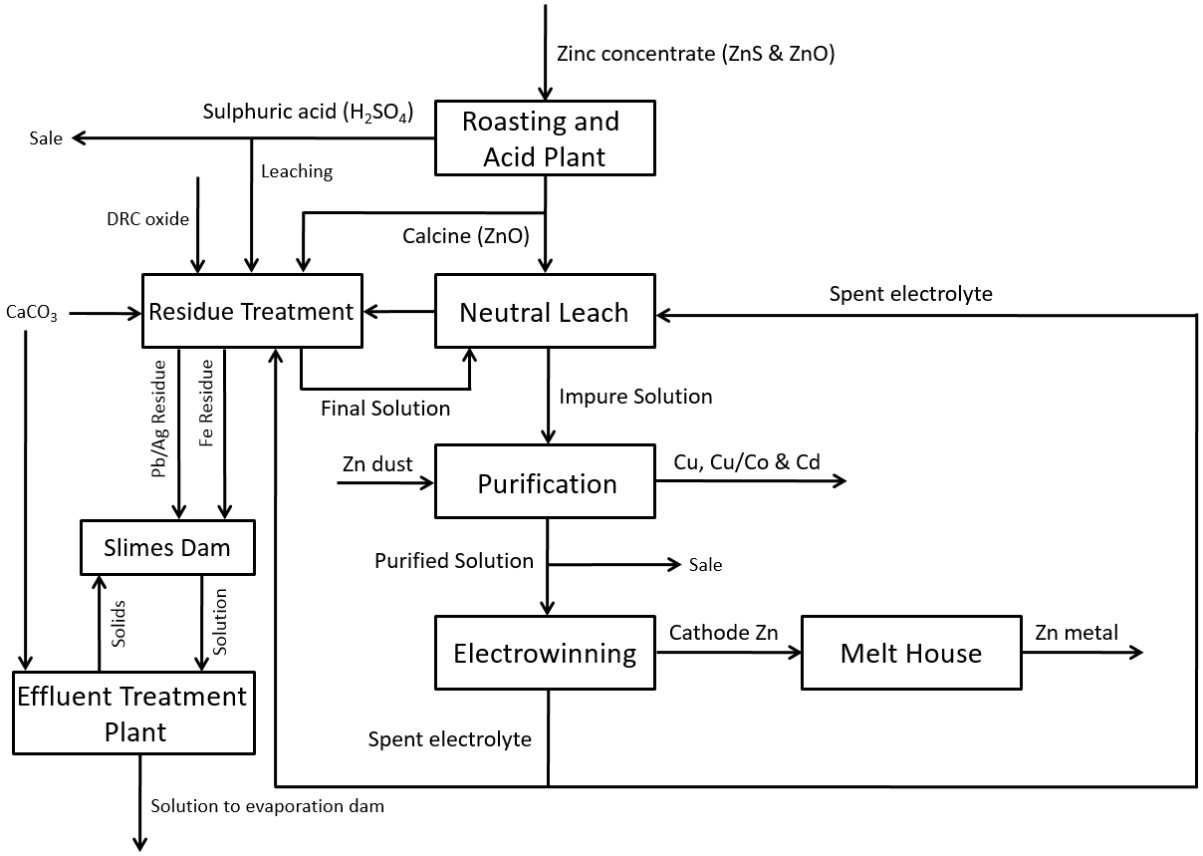


FIGURE 1: A SIMPLIFIED FLOW SHEET OF THE ZINCOR PROCESS

The Purification Plant removed impurities such as copper, cobalt, nickel and cadmium in three stages through a cementation reaction with zinc dust. The resulting copper and copper-cobalt cakes were treated to upgrade the copper content and recover some zinc before being sold. The cadmium cakes were not easily saleable and were stored in bunkers. The zinc-rich solution exiting the Purification Plant contained only very small amounts of impurities and was known as Purified Solution. This solution reported to the Cell House where the zinc was plated onto aluminium cathodes through an electrowinning process. At times some of this solution was sold to the agricultural industry. The electrolyte exiting the Cell House was known as Spent Electrolyte. Since sulphuric acid was generated in the electrolytic cells, the spent electrolyte contained approximately 150 g/l H_2SO_4. The acidic spent electrolyte was used for leaching in the Neutral Leach and Residue Treatment plants.

The metallic zinc was manually stripped from the cathodes every 24 hours and sent to the Melt House for melting and casting. The zinc dust used for cementation in the Purification Plant was also produced in the Melt House.

1.2.2. RESIDUE TREATMENT PLANT PROCESS DESCRIPTION:

The residual zinc found in the Neutral Leach residue was attributed to the presence of insoluble zinc ferrites in the calcine, which were formed during roasting. The Zincor calcine contained up to 15 % of these zinc ferrites, which did not leach under the conditions maintained in the Neutral Leach circuit. This phenomenon contributes to one of the biggest problems in the zinc industry in that only the zinc oxide is readily soluble, while other forms require hot concentrated acid [TU Delft, 2001]. Zinc ferrites have been found to be soluble in solutions containing in excess of 100 g/l H_2SO_4 and at temperatures of 90 to 95 ^oC [Ramachandra Sarma *et al*., 1976 as quoted by Claassen *et al*., 2002]. Nearly complete dissolution of both zinc and iron can be achieved at operating temperatures exceeding 90 ^oC [Berndt *et al*., 1991]. The Residue Treatment Plant operated at the aggressive conditions required to recover this residual zinc. This plant was not part of the original Zincor circuit. The Hot Acid Leach (HAL) and Iron Removal circuits were commissioned in 1976, with the Super Hot Acid Leach (SHAL) being added in 1984 to accommodate the additional residue loading associated with increased plant capacity. The complete Residue Treatment Plant was hot-commissioned in May 2002.

A simplified flow sheet of the Residue Treatment Plant can be seen in *Figure 2*. The operation consisted of three leach stages and an iron removal stage. The leach stages included the Weak Acid Leach (WAL), HAL and SHAL. The leaching conditions became more aggressive with each stage, i.e. the temperature and acidity were increased. Heating in the Residue Treatment Plant was accomplished with the injection of steam from the Acid Plant boilers. The leach stages were operated in a counter-current manner with the thickener underflow from each stage progressing to the next stage, while the thickener overflow returned to the preceding stage.

THE WEAK ACID LEACH STAGE:

The WAL was the first of the leaching stages. Here the Neutral Leach residue was mixed with acidic spent electrolyte to maintain an acidity of between 8 and 12 g/l of H_2SO_4 and a temperature of approximately 55 to 65 ^oC. The overflow solution from the HAL stage was also added here. The continuous leach was followed by a thickening stage. The thickener overflow solution contained all the dissolved zinc and iron and was known as Hot Iron Solution (HIS) and reported to the Iron Removal

Stage for the removal of the iron impurities. The thickener underflow proceeded to the HAL stage for further treatment.

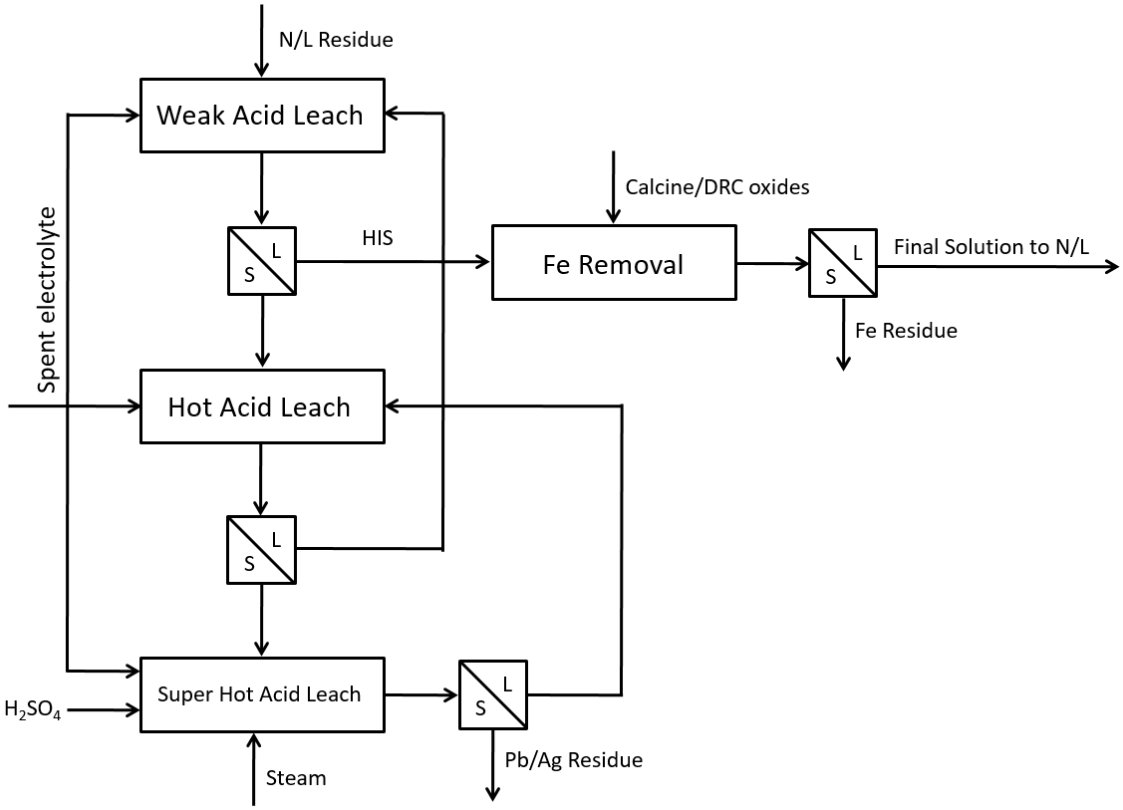


FIGURE 2: A SIMPLIFIED FLOW SHEET OF THE RESIDUE TREATMENT PLANT

THE HOT ACID LEACH STAGE:

The HAL stage consisted of three 100 m^3 reactors in series. Spent electrolyte was added into the first reactor to maintain a free acid concentration of 40 to 60 g/l. Steam from the Acid Plant boilers was also injected here to maintain a temperature of approximately 80 ^oC. It was estimated that between 60 to 70 % of the residual zinc ferrites in the Neutral Leach residue was dissolved during the HAL stage. The zinc in solution was present as zinc sulphate and the iron as ferric sulphate. The leaching in the HAL stage took place according to *Reaction 1*:

$$ZnO.Fe_2O_3 + 4H_2SO_4 \rightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O \qquad (1)$$

The slurry from the HAL stage was thickened, with the overflow reporting to the WAL stage and the underflow reporting to the SHAL stage for further treatment.

THE SUPER HOT ACID LEACH STAGE:

The SHAL stage consisted of four 60 m^3 tanks in series. Both spent electrolyte and concentrated sulphuric acid were added to achieve an acidity of between 90 to 100 g/l of H_2SO_4. The addition of concentrated acid had to be limited at times, depending on the sulphate balance in the overall plant circuit. To be in a position to add more concentrated acid the bleed volumes had to be increased significantly. While steam was used for heating, the addition of concentrated shulphuric acid also generated heat, so that the final temperature in the SHAL stage was approximately 90 ^oC. Almost all of the remaining undissolved zinc was leached during the SHAL stage.

Due to incomplete roasting, the calcine contained a small portion of zinc sulphide (ZnS). During the SHAL stage the zinc sulphide reacted with the ferric sulphate in solution to form ferrous sulphate, zinc sulphate and sulphur. This occurred according to *Reaction 2*:

$$Fe_2(SO_4)_3 + ZnS \rightarrow 2FeSO_4 + ZnSO_4 + S \qquad (2)$$

This reaction was responsible for the high ferrous levels in the HIS and subsequently in the iron thickener overflow, known as Final Solution.

The slurry from the SHAL stage was thickened. The overflow reported to the HAL stage, while the thickener underflow was filtered on a horizontal vacuum belt filter to recover the zinc-rich filtrate. The filtrate was returned to the SHAL thickener, while the cake was re-pulped and pumped to the residue disposal site. This residue contained $PbSO_4$, Jarosites (plumbo and argento) with small amounts of silver and was known as the lead-silver (Pb/Ag) residue.

THE IRON REMOVAL STAGE:

Due to the aggressive leaching conditions in the Residue Treatment Plant, most of the zinc ferrite was dissolved, so that the overflow solution from the WAL stage contained dissolved zinc and between 15 and 30 g/l of iron. Because of the presence of dissolved iron this solution was known as Hot Iron Solution (HIS). Most of the iron was in the ferric form with a small amount of ferrous iron.

The presence of iron interfered with the zinc dust purification process, decreased the current efficiency, increased the rate of anode corrosion and resulted in lead and iron impurities in the cathode zinc. To produce a high-grade zinc product required iron levels lower than 5 mg/l in the

Purified Solution. Iron removal was necessary, not only to maintain a high quality zinc product, but to avoid circulating loads of iron.

The iron was removed from the zinc-rich solution by precipitating it as an oxide, oxy-hydroxide or hydroxyl salt. The patented Zincor Iron Removal Stage was similar to the so-called Para-goethite Process and was developed over a period of thirty years. The process consisted of six 60 m^3 stirred reactors in series with an overflow between each tank. Roaster calcine and zinc oxide fume were utilised as neutralising agents. The zinc oxide fume used at Zincor originated from a copper-cobalt smelting operation in the Democratic Republic of Congo (DRC) and was known on the plant as DRC oxide.

The calcine was slurried with iron thickener overflow solution to an SG (specific gravity) of 1.35 to 1.4. The DRC oxide was slurried with process water to a density of 1.3. The two neutralising agents were fed at a constant rate, while the HIS addition rate was automatically controlled to maintain a slurry pH of 3.2 in the first reactor. The dissolution of the zinc oxide raised the pH of the solution high enough to allow for the precipitation of the iron in solution. Between 85 and 90 % of the zinc in the zinc oxide was dissolved and up to 80 % of the iron was precipitated in one pass [Meyer *et al*., 1996].

Heating was done by circulating slurry from the first reaction tank through a spiral heat exchanger to achieve a temperature of 65 ^{o}C. Unfortunately the heat exchanger had to be taken off-line regularly for cleaning, due to scaling with Jarosite.

Only the iron in the ferric form precipitated out, while the ferrous iron remained in solution. The ferrous iron was converted back to ferric iron in the Neutral Leach circuit by adding manganese dioxide (MnO_2). The MnO_2 originated from cell cleaning in the electrowinning circuit. The conversion from ferrous to ferric iron occurred according to *Reaction 3*:

$$2FeSO_4 + MnO_2 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + 2H_2O \qquad (3)$$

An acid wash was done in the second reactor by adding more HIS to reduce the pH to 3. The acid wash served two purposes. Firstly, it dissolved any unleached or entrained zinc oxide and leached any zinc sulphates that may have formed. Secondly, the iron provided by the re-dissolution of Ferrihydrite, together with that contained in the HIS, provided the cement required for the hydrolysis reaction. A pH of less than 2.5 resulted in the formation of silica gel, making filtration of the precipitate very

difficult. Further reaction between residual neutralising agents and HIS took place in the downstream reactors, resulting in a final pH of approximately 3.4 in the thickener overflow solution. Claassen, 2005 found that the acid wash step resulted in some Ferrihydrite particles being dissolved and re-precipitating as Ferrihydrite and Schwertmannite. Schwertmannite is denser than Ferrihydrite and contains less insoluble zinc.

The slurry from the Iron Removal Stage was thickened. The overflow solution was rich in zinc and contained small amounts of iron. It was known as Final Solution and was sent back to the Neutral Leach circuit for zinc recovery. The thickener underflow was filtered on a horizontal vacuum filter in order to recover the zinc-rich filtrate. The belt filters could maintain the soluble zinc losses at or below an average of 1% at a wash ratio of 2.1 [Claassen *et al.*, 2002]. The filtrate was returned to the circuit and the cake, known as iron (Fe) residue, was re-pulped and sent to the residue disposal site where it was landfilled.

1.3. PROBLEM STATEMENT:

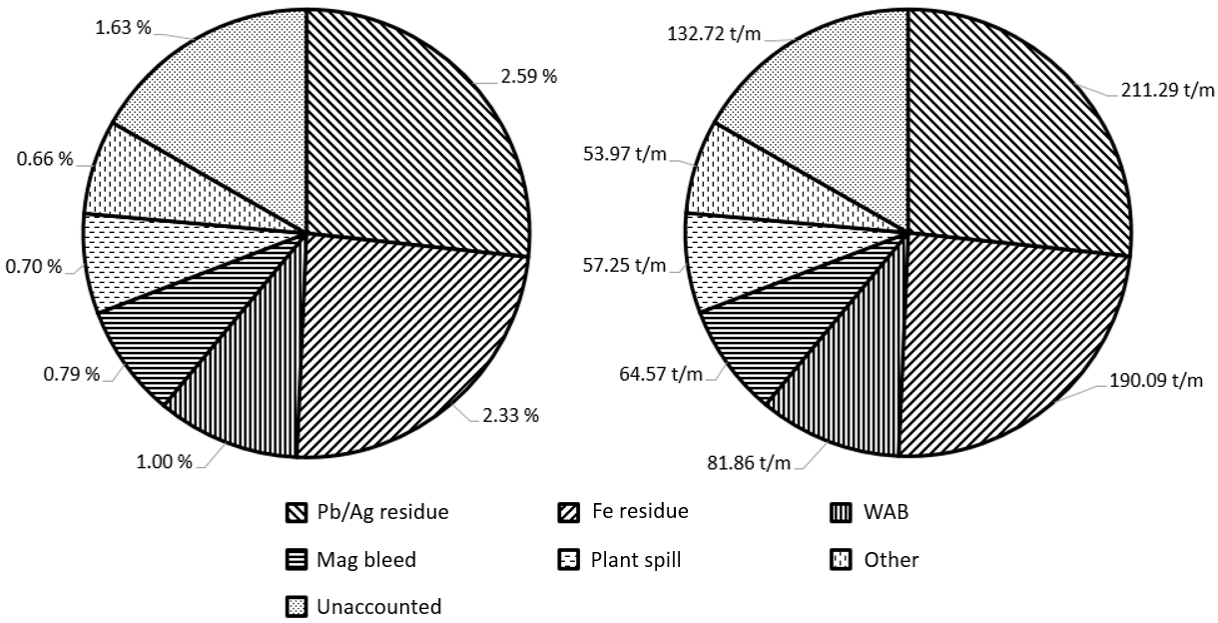
One of the major factors that influence the zinc recovery is the particular iron removal technology in use. Due to the limitations of Zincor's iron removal technology the maximum achievable zinc recovery was 94 %, which was well below the industry standard of 96 % [Claassen *et al*., 2002]. The average recovery achieved during the period of 1 January 2009 to 30 September 2011 was 90.29 %, with the zinc losses amounting to 9.71 %. *Figure 3* gives a breakdown of the biggest contributors to the zinc losses at that time.

The major losses were those through the weak acid and magnesium bleed streams, plant spillages, unaccounted losses and the Residue Treatment Plant residues, namely the Pb/Ag and Fe residues. The 'other' losses were made up of handling losses and losses through the gypsum residue and cell cleaning, as well as a number of other minor losses, such as zinc contained in the Purification Plant residues (the Cu, Cu/Co and Cd cakes).

BLEED LOSSES:

The purpose of the Magnesium Bleed Plant was to bleed manganese, magnesium and sulphates from the circuit, as well as to assist with solution inventory control. A portion of the spent electrolyte stream was bled to the Magnesium Bleed Plant at a rate of approximately 10 m^3/hour, where slaked lime was added to increase the pH to between 6 and 7, so that zinc was precipitated out. The bulk of the

magnesium, manganese and sulphates remained in solution, while the zinc reported to the cake, together with a large amount of gypsum. The cake was returned to the circuit via the HAL and SHAL stages to recover the zinc. The presence of gypsum aided filtration on the Pb/Ag belt. The solution stream reported to the Effluent Treatment Plant where it was treated and sent to the disposal facility.



<u>FIGURE 3:</u> A BREAKDOWN OF THE BIGGEST CONTRIBUTORS TO THE ZINC LOSSES FOR THE PERIOD OF 1 JANUARY 2009 TO 30 SEPTEMBER 2011 (TOTAL Zn LOSSES = 9.71 % OR 792 t/month)

The losses through the WAB occurred as a result of residual calcine in the gas train of the Acid Plant. Gas scrubbing removed the bulk of the calcine solids and other impurities, but some residual calcine remained. The gas was cooled and converted to a weak acid, which leached the calcine. The weak acid stream, now containing dissolved zinc, was pumped to the Effluent Treatment Plant for neutralisation before disposal.

PLANT SPILLAGES:

The losses through plant spillages occurred when tanks and sumps overflowed. These streams reported to the Effluent Treatment Plant where the solution was neutralised and pumped to the residue disposal site. Once zinc had reported to the Effluent Treatment Plant it was lost to the disposal facility and could not be recovered.

UNACCOUNTED LOSSES:

The unaccounted losses could be attributed to measurement errors, particularly in the secondary products like the Cu, Cu/Co and Cd cakes from the Purification Plant, as well as the zinc dross and metallic scrap from the smelting operation.

RESIDUE LOSSES:

Two residues exited the operation via the Residue Treatment Plant. The Fe residue originated from the Iron Removal Stage and the Pb/Ag residue from the SHAL stage (refer to *Figure 2* for the simplified flow sheet of the Residue Treatment Plant). The zinc losses through the residues were divided into a soluble and insoluble portion. The soluble zinc losses were a function of the filterability of the residue, while the insoluble zinc losses were a function of the leaching conditions, particularly the type of neutralising agent in use, temperature, acidity and residence time.

Referring back to *Figure 3*, the zinc losses through the Pb/Ag residue made up the biggest portion of the total losses at 2.59% (or an average of 211 t/month). This amounted to 26.68 % of the total losses (or just over a quarter). The losses through the Fe residue amounted to 2.33 % (or an average of about 190 t/month). This contributed 24 % to the total zinc losses (or almost a quarter). *Figure 4* gives a breakdown of the zinc losses through the Residue Treatment Plant residues.

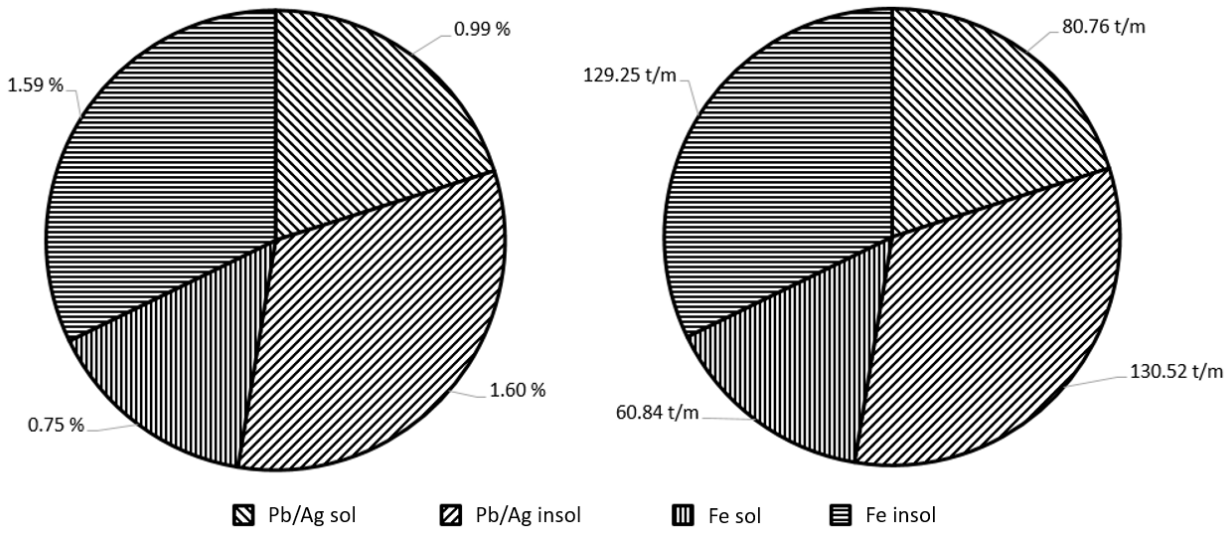


FIGURE 4: A BREAKDOWN OF THE ZINC LOSSES (SHOWN HERE IN % AND t/month) THROUGH THE RESIDUE TREATMENT PLANT RESIDUES FOR THE PERIOD OF 1 JANUARY 2009 TO 30 SEPTEMBER 2011

LOSSES THROUGH THE Pb/Ag RESIDUE:

Concentrated sulphuric acid and spent electrolyte were used for leaching in the SHAL stage. Acid addition was at times limited due to an imbalance in the sulphate concentration in the overall circuit. Steam from the boilers was injected for heating. However, steam supply was sometimes interrupted by unforeseen events, so that the desired temperature was not maintained consistently. If the SHAL stage was not operated at the desired pH and temperature profile, incomplete zinc leaching and high insoluble zinc losses resulted. The insoluble zinc loss amounted to 1.60 % or 130.52 t/month. This residue also tended to be difficult to filter, so that the soluble losses were 0.99 % compared to only 0.75 % through the Fe residue. An improvement had been noted since the addition of the Basic Zinc Sulphate cake (from the Magnesium Bleed operation) into the HAL and SHAL stages to aid filtration.

LOSSES THROUGH THE Fe RESIDUE:

The insoluble losses in the Fe residue could be attributed to the use of calcine and DRC oxide (both zinc-rich neutralising agents) for neutralisation. The insoluble zinc ferrite portion of the calcine did not leach under these operating conditions and iron precipitate coated unleached neutralising agent. At 1.59 % (or 129.25 t/month) the insoluble zinc loss through the Fe residue was the second biggest contributor to the overall zinc losses.

THE IMPLEMENTATION OF ZINC OXIDE FUME AS A NEUTRALISING AGENT:

Prior to May 2007 only calcine was used as a neutralising agent in the Iron Removal Stage. During May 2007 DRC oxide was added to supplement calcine during a roaster rebuild and as a recovery improvement initiative. This oxide was similar to calcine, but contained very little iron. The zinc content of DRC oxide was 69.30 % (the average for the period of 1 January 2009 to 30 September 2011), with an iron content of 0.74 % compared to 6.33 % for calcine. The plant trial resulted in a recovery improvement from 90.30 % to 92.60 % [Wyethe *et al*., 2008]. These positive results prompted the permanent use of DRC oxide as a supplement to calcine.

Figure 5 compares the zinc losses from prior to DRC oxide addition to the losses after the implementation of DRC oxide addition. The periods in question are 1 January 2006 to 31 May 2007 and 1 January 2009 to 30 September 2011 (when the DRC oxide was added consistently). The average recovery for the period of 1 January 2006 to 31 May 2007 was 90.30 %. During this period the zinc losses (both soluble and insoluble) through the Fe residue amounted to 4.66 %, which made up about half of the total zinc losses. The insoluble zinc losses alone were as high as 3.20 %, which made up a third of the total zinc losses.

The results from the period of 1 January 2009 to 30 September 2011 showed a significant decrease in the losses through the Fe residue. The insoluble portion decreased by 50 % with the addition of DRC oxides. Sadly, while the zinc losses through the Fe residue decreased, an increase in losses was seen in other areas, so that the average overall zinc recovery during this period was only 90.29 %.

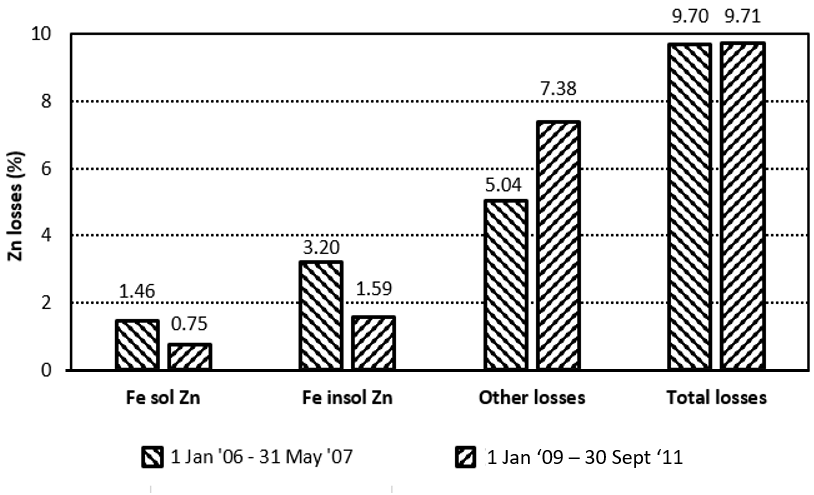


FIGURE 5: COMPARISON OF ZINC LOSSES FROM BEFORE AND AFTER THE IMPLEMENTATION OF DRC OXIDE AS A SUPPLEMENT TO CALCINE IN THE ZINCOR IRON REMOVAL STAGE

The improvement seen since the addition of DRC oxides prompted a number of attempts to increase the DRC oxide addition in the hope of eventually replacing calcine. However, poor filtration was experienced each time the amount of oxides was significantly more than the calcine. There seemed to be an 'ideal' ratio of DRC oxides:calcine to ensure reasonable settling and filtration of the precipitate. While the zinc ferrite complex contained in the calcine contributed to the high insoluble zinc losses through the iron residue, it seemed to act as a form of iron seed that promoted particle growth and was essential to achieving good settling and filtration. Since the iron content in the DRC oxides was very low, excessive use of it as a neutralising agent depleted the seed necessary for the formation of a precipitate with good dewatering characteristics.

Hence, there was scope for improvement when it came to reducing the insoluble zinc loss through the iron residue by focusing on the type of neutralising agent in use and the implementation of seeding. The incentive was that a reduction of 1 % in the insoluble zinc loss in the iron residue translated to an overall zinc recovery improvement of 0.25 % [Wyethe *et al.*, 2008].

1.4. OBJECTIVES:

The goal of this work was to further reduce the losses through the iron residue. It was seen in *Section 1.3* that the insoluble zinc losses through the Fe and Pb/Ag residues made up the biggest portion of the total zinc losses. The insoluble losses through the Fe residue were attributed to the presence of insoluble zinc ferrite in the calcine, as well as coating of unleached zinc-rich neutralising agent (both calcine and DRC oxide) by iron precipitate. The first objective was to further reduce the insoluble zinc losses by increasing the DRC oxide addition in order to benefit from the low iron content (i.e. insoluble zinc ferrite content). Added to this, alternative neutralising agents that contained little or no zinc would also be considered as replacements of the traditional zinc-rich neutralising agent.

The secondary objective was to reduce the soluble zinc losses by improving the filterability of the precipitate product.

The introduction of a seed recycle could potentially address both the primary and secondary objectives. Firstly, the presence of seed could reduce insoluble zinc losses by providing additional surface area, or precipitation sites, for iron to precipitate onto. This could result in less coating of unleached zinc-rich neutralising agent. Secondly, the presence of seed could reduce the soluble zinc losses by promoting agglomeration growth of particles and the formation of a denser precipitate, thereby improving the dewatering characteristics of the precipitate product.

1.5. SCOPE OF WORK:

The work included a review of literature, laboratory experiments and a plant trial.

Preliminary laboratory work was carried out to determine a working experimental procedure and to identify appropriate alternative neutralising agents to supplement or replace calcine. The final laboratory work evaluated the chosen alternative neutralising agents, together with a seed recycle.

The work concluded with a plant trial. Since the alternative neutralising agents identified in the laboratory work could not be evaluated on a plant scale without major plant modifications, the trial focused only on the implementation of a seed recycle.

1.6. THESIS LAYOUT AND STRUCTURE:

The next chapter consists of the literature review, which includes a discussion of iron removal in the zinc industry, a summary and comparison of iron removal technologies, general precipitation theory and principles and the key parameters to be considered in iron precipitation.

The remainder of the document is divided into two major chapters, namely the laboratory work and the plant trial. Each of these chapters contains a section on methodology and results and discussion.

The closing section summarises the main findings and observations and attempts to draw some overarching conclusions. It also includes some recommendations.

2. LITERATURE REVIEW:

2.1. IRON REMOVAL IN THE ZINC INDUSTRY:

Sphalerite (ZnS) is the principal zinc ore mineral. Impurities can substitute zinc in the mineral lattice of Sphalerite and have a significant impact on the metallurgical performance of a typical zinc refinery. Marmatite [(Fe,Zn)S] forms when iron replaces zinc in the Sphalerite structure. Zinc concentrates typically contain between 3 and 14 % iron, with the world average at approximately 8 % [TU Delft, 2001]. The iron is present as Pyrite (FeS_2), Pyrrhotite (FeS) and Chalcopyrite ($CuFeS_2$) [Ashman, 1999]. The iron content in Sphalerite ore tends to increase with increasing temperature of formation in the ore body.

During the roasting operation some of the iron combines with the zinc to form zinc ferrite, also known as Franklinite. Zinc ferrite formation occurs according to *Reaction 4* [Ashman, 1999]:

$$2FeS + ZnS + 5O_2 \rightarrow ZnO.Fe_2O_3 + 3SO_2 + heat \qquad (4)$$

Zinc ferrite commonly occurs as tiny crystals and is insoluble under atmospheric leach conditions. Zinc loss characteristic of iron removal in the zinc industry is largely attributed to the presence of zinc ferrite and has an almost linear relationship with the iron content of the zinc concentrate [Meyer *et al*., 1996]. Elevated temperatures and acid strength are required to dissolve the zinc ferrite. Under these aggressive conditions both the zinc and iron are leached. The iron needs to be removed from the leach liquor, since it has an adverse effect on the zinc operation, particularly on the current efficiency in the electrowinning circuit.

The amount of iron residue produced globally in the zinc industry is between $^1/_6$ and $^1/_3$ of the zinc tonnage [Loan *et al*., 2005]. Precipitation is the most common means of removing iron from solution. Various iron compounds are precipitated, depending on the chosen iron removal technology [TU Delft, 2001]. The precipitation reaction occurs by contacting the solution rich in iron and zinc with a neutralising agent, commonly a zinc oxide. The inherent weakness of most commercial iron removal technologies is the high undissolved zinc loss associated with the use of a zinc-rich neutralising agent. Zinc losses occur through adsorption of zinc onto the precipitate, coating of unleached neutralising agent with precipitate and the entrainment of zinc sulphate solution in the amorphous precipitate and unleached ferrites.

While the iron residue is one of the biggest contributors to the zinc losses, it does have the advantage of aiding in solution purification [Claassen *et al.*, 2003]. Impurities such as halides, arsenic, antimony, copper, nickel, manganese and cobalt are all rejected through the iron residue [Dutrizac, 1980 as quoted by Claassen *et al*., 2002]. Under favourable conditions each mol of dissolved iron will carry almost a mol of impurity into the residue [Phillips, 1958]. The iron residue also acts as SO_4 bleed.

Wyethe *et al*. (2008) studied Zincor's capacity for halide rejection after implementing the use of zinc oxide fume as a neutralising agent in the Iron Removal Stage. The study showed that the magnesium bleed operation sufficiently rejected chlorides. Approximately 70 % of the fluoride was rejected via the iron residue, with up to 27 % rejected via the lead silver residue. It was determined that the fluoride rejection capacity via the iron residue with a fluoride solution content of 2 – 4 mg/L was between 0.14 to 0.19 kg F/t Fe residue.

Unfortunately, the zinc losses associated with iron far outweigh any of the benefits. The presence of some of these impurities in the precipitate also make it an environmental concern. To maximise zinc recovery and minimise the environmental impact some residues can be regarded as secondary sources of zinc and may require further treatment [TU Delft, 2001].

There are a number of different iron removal technologies, including the Hematite, Jarosite, Goethite, Para-goethite and Zincor processes. The ideal process has a low capital and operating cost and achieves an optimal zinc recovery, while producing a residue that is environmentally stable and potentially saleable [Claassen, 2005]. None of the technologies currently available meet these criteria and each process has limitations. A brief discussion of each of the iron removal technologies can be found in *Section 2.1.2.*

2.1.1. THERMODYNAMICS OF IRON REMOVAL:

Figure 6 is a stability diagram defining the conditions for the precipitation of different iron phases with respect to temperature and pH. From it one can determine the operating conditions required to generate a particular iron residue.

The Zincor Iron Removal Stage operates at a pH of between 3 and 3.2, a temperature of 60 ^{o}C and a ferric iron and sulphate concentration of between 0.1 and 0.05 % (by mass). Within these operating parameters goethite is expected to be the thermodynamically stable iron complex.

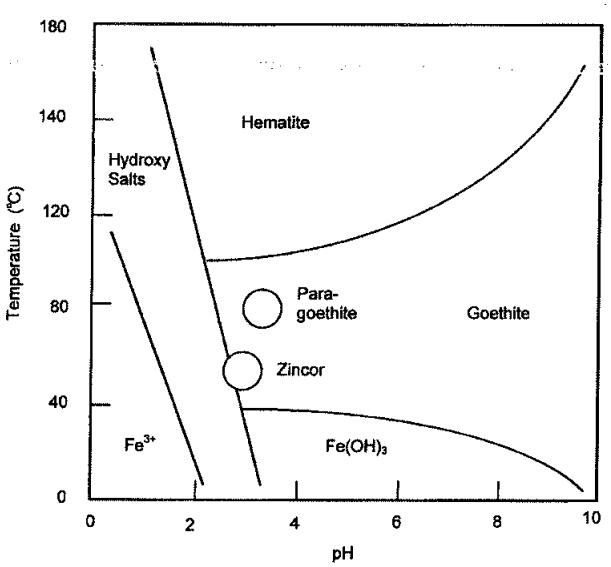


FIGURE 6: CONDITIONS FOR THE PRECIPITATION OF HEMATITE, GOETHITE, FERRIC HYDROXIDE AND HYDROXY SALTS (INCLUDING JAROSITES) FROM 0.5M FERRIC SULPHATE SOLUTION [ADAPTED BY CLAASSEN et al., 2002 FROM BABCAN, 1971]

When operating outside of equilibrium conditions metastable phases, such as Ferrihydrite and Schwertmannite, are produced [Claassen and Sandenbergh, 2006].

2.1.2. COMMERCIAL IRON REMOVAL PROCESSES:

THE JAROSITE PROCESS:

The Jarosite process was developed in 1964 and was the first iron removal technology that made the production of a filterable iron residue possible on a commercial scale [Van Niekerk and Begley, 1991]. Unfortunately the residue is voluminous and has no further value or potential use. Since this technology is low cost (if one excludes the residue disposal costs), simple to operate and achieves a filterable product, it is still the most widely used iron removal process in the zinc industry today.

Iron is mainly precipitated in the form of ammonium Jarosite, which is defined by *Reaction 5*:

$$3Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 12H_2O \rightarrow 2[(NH_4)Fe_3(OH)_6(SO_4)_2] + 6H_2SO_4 \quad (5)$$

The reaction generates a large amount of acid. The majority of the neutralising agent is used to neutralise the acid generated by the precipitation reaction, which contributes to high insoluble zinc losses [Sinclair, 2005].

Most commercial Jarosite processes are based on sodium or ammonium Jarosite and almost all Jarosite residues contain amounts of Ag, Pb and Tl. In fact, Jarosite is widely known as a means of rejecting thallium from a zinc operation [TU Delft, 2001]. The Jarosite residue also provides an outlet for sulphate. The composition of the Jarosite residue will depend on the flow sheet used and the separation of a lead-silver residue. Industrial Jarosite residues typically contain 30 % iron and 5 % zinc [Sinclair, 2005].

There have been a number of modifications to the technology since it was first established, including multiple stage leaching, lead-silver recovery, pre-neutralisation and an acid wash of the precipitate. The pre-neutralisation step aims to reduce the residual acidity in the hot acid leach solution in a separate stage, from which the residue can be separated for subsequent zinc recovery. The acid wash of the precipitate aims to recover zinc. The Jarosite is stable at these operating conditions so that it is possible to separate the zinc from the residue. Two of the most notable variations to the traditional Jarosite process include the Dor Variant and the Outokumpu Conversion processes [Sinclair, 2005].

THE GOETHITE PROCESS:

This process was developed in the mid-sixties to early seventies. It was the second of the iron removal technologies to be developed and came about after it was discovered that the use of hot dilute solutions kept the supersaturation level relatively low and resulted in the formation of coarse particles that filter well [Claassen *et al.*, 2003]. Goethite precipitate has a lower zinc content and higher bulk density than Jarosite. The Goethite process is simpler to operate than the Jarosite process, but it is more costly. Similar to the Jarosite process, it has the ability to remove other unwanted impurities along with the iron.

The ferric iron concentration of the solution is usually around 30 g/l, but needs to be maintained at around 2 g/l to ensure good settling and filtration characteristics of the Goethite precipitate. This is achieved by reducing iron to the ferrous state with zinc sulphide concentrates and then re-oxidising it with air. This is the basis of Goethite precipitation and was developed by Vieille Montagne at the Balen smelter [Andre and Masson, 1973; and Bellefroid, 1985 as quoted by Sinclair, 2005]. The process follows *Reaction 6:*

$$2FeSO_4 + {}^1/_2O_2 + 3H_2O \rightarrow 2FeO.OH + 2H_2SO_4 \qquad (6)$$

The reaction generates a large amount of acid that needs to be neutralised, typically by a zinc-rich neutralising agent, contributing to the insoluble zinc losses [Sinclair, 2005].

As with the Jarosite residue, the Goethite residue presents some concerns in terms of environmental management and rehabilitation. Pyrometallurgical treatment of the residue may address some of these issues by recovering the contained zinc and stabilising the residue, making it potentially saleable. However, the addition of this process to a zinc refinery requires a high capital investment. An alternative to a pyrometallurgical solution is to mix the washed Goethite residue with steel plant slag, lime and possibly concrete to form a product which cures to a stable and compact material after a few days. The mixture is formed into a synthetic gravel for use in the construction industry and appears to be environmentally acceptable [TU Delft, 2001].

The Goethite process continues to advance and may expand at the expense of the Jarosite process [TU Delft, 2001].

THE PARA-GOETHITE PROCESS:

The Para-goethite process is a variation of the Goethite process and is a simple and low cost solution that is still in operation today. The process was developed by the Electrolytic Zinc Company of Australasia as the Electrolytic Zin (EZ) Ferric Oxide Process, but is generally referred to as the Para-goethite process. This process is also in operation at the Pasminco refinery in Hobart and operates in conjunction with a 'co-treatment strategy', where the residue is further treated in lead sintering [Loan *et al*., 2005]. The para-goethite precipitation occurs according to *Reaction 7:*

$$Fe_2(SO_4)_3 + 4H_2O \rightarrow 2FeO.OH + 3H_2SO_4 \qquad (7)$$

Zinc-rich neutralising agent is used to neutralise the sulphuric acid generated during precipitation, which contributes to the high insoluble zinc losses characteristic of this process.

The Para-goethite process is a simplification of the Goethite process by eliminating the iron reduction stage. However, this is done at the expense of increased quantities of residue and increased zinc losses. The precipitation is carried out in a single stage rather than a series of tanks. Hence, large tanks, or a number of single tanks operating in parallel, are generally used. As with the Goethite process, a low ferric iron concentration is desirable. This is difficult to maintain in practice, so that the iron precipitate formed is not pure Goethite. Studies have shown that the residues from the Para-goethite

and Zincor processes contain Ferrihydrite and Schwertmannite [Loan *et al*., 2006; Claassen *et al.*, 2002], which are both metastable toward Goethite. The iron content ranges between 33 and 35 % and the zinc content between 10 and 15 %. While this process is less efficient than the other processes in terms of zinc recovery, it is one of the cheapest and easiest to operate [Meyer *et al*., 1996].

Pyrometallurgical treatment of the Para-goethite residue will recover zinc and other valuable metals. This has been done at the electrolytic zinc plant of the Porto Vesme smelter in Sardinia and the Zinifex Limited Hobart smelter [Sinclair, 2005].

THE ZINCOR PROCESS:

The Zincor process, which was similar to the Para-goethite process, was unique and developed and patented by Zincor [South African Patent Application No. 75/27/37, April 1, 1976]. It employed a unique pH profile, with an acid wash in the second reactor. This stage-wise precipitation distinguished the Zincor process from all others. The detailed process description can be found in *Section 1.2.2.*

Goethite was expected to be present in the Zincor residue (refer to *Figure 6*). Claassen *et al*., 2002 and 2007 identified distinct phases that were poorly crystalline, contained high levels of impurities and were metastable toward Goethite. The transformation to Goethite was probably hindered by the presence of impurities, such as silica. The following phases were identified in the Zincor residue:

- 45% Schwertmannite ($Fe_8O_8(OH)_6SO_4$),
- 5% Ferrihydrite ($Fe_5O_7(OH).4H_2O$),
- 20% Plumbo-Jarosite ($Pb[Fe_3(SO_4)_2(OH)_6]_2$),
- 25% Franklinite ($ZnO.Fe_2O_3$) and
- 5% of an unknown poorly crystalline phase.

The Jarosite was present as plumbo-Jarosite due to the occurrence of lead in the Zincor circuit.

Claassen proposed that the iron was removed according to *Reactions 8, 9* and *10* (in order of importance):

$$4Fe_2(SO_4)_3 + ZnO(s) + 13H_2O \rightarrow Fe_8O_8(OH)_6SO_4(s) + ZnSO_4 + 10H_2SO_4 \quad (8)$$

$$3Fe_2(SO_4)_3 + PbSO_4(s) + ZnO(s) + 11H_2O \rightarrow 2Pb_{0.5}Fe_3(SO_4)_2(OH)_6(s) + ZnSO_4 + 5H_2SO_4 \quad (9)$$

$$5Fe_2(SO_4)_3 + ZnO(s) + 23H_2O \rightarrow 2[Fe_5O_7(OH).4H_2O](s) + ZnSO_4 + 14H_2SO_4 \quad (10)$$

THE HEMATITE PROCESS:

The Hematite process is in operation at the Iijima Electrolytic Zinc Plant near Akita in Japan. The iron is precipitated as an iron oxide in the presence of oxygen, at a high temperature and pressure of approximately 200 ^{o}C and 2 MPa, respectively. There is a reduction step to convert the iron to the ferrous state. Keeping a low solution ferric iron concentration ensures the formation of almost pure hematite. Hematite formation occurs according to *Reaction 11* [Sinclair, 2005]:

$$2FeSO_4 + 2H_2O + {}^{1}/_{2}O_2 \rightarrow Fe_2O_3 + 2H_2SO_4 \qquad (11)$$

The reaction results in the generation of acid, which is neutralised with zinc oxide and limestone, resulting in the formation of a clean and saleable gypsum product [TU Delft, 2001].

Hematite is thermodynamically stable at all temperatures, has a low water content and is the most compact and stable of all the iron residues. The volume of hematite residue is less than half of the residue produced by any other iron removal process. Hematite has an iron content of between 55 and 60 %, a zinc content of approximately 1 % and a density in excess of 4 t/m^3. While the impurity content in hematite residues render it unsuitable for use in the iron and steel making industries, it could have commercial applications in the cement manufacturing and pigmenting industries [Sinclair, 2005].

This process is the most favourable in terms of zinc recovery, residue disposal and environmental liabilities. However, the elevated temperature and pressure required result in high operating costs. In addition, the capital investment is almost double that needed for the Jarosite or Goethite processes [TU Delft, 2001].

2.1.3. COMPARISON OF COMMERCIAL IRON REMOVAL PROCESSES:

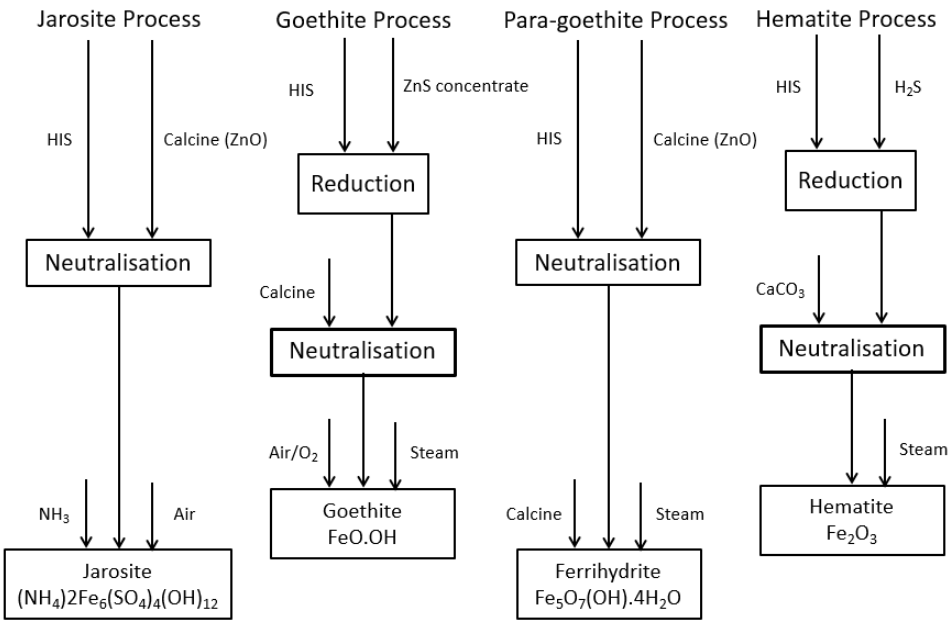
A desirable iron removal technology possesses the following qualities [TU Delft, 2001]:

- The process produces a precipitate with good dewatering and materials handling characteristics;
- The process produces a precipitate that contains very little zinc or other valuable elements;
- The process produces a precipitate that is stable, compact and potentially saleable;
- The process easily integrates with the rest of the zinc circuit;
- The process has a low capital investment and operating cost; and
- The process acts as a purification step by also removing other unwanted impurities.

The Jarosite, Goethite, Para-goethite and Zincor processes are robust and simple to operate and have a low capital requirement and operating cost. However, their residues are voluminous so that they are difficult to manage environmentally. Their disposal and rehabilitation costs are high, with the Para-goethite process being the least competitive.

The Hematite process is the most attractive in terms of zinc recovery and the residue is compact and stable. However, the capital requirement and operating cost are the highest of all the available technologies. The cost does not compare favourably, unless there is potential for the hematite residue to be saleable [Sinclair, 2005].

The type of iron removal technology determines the achievable zinc recovery. A comparison of the most common iron removal technologies can be seen in *Figure 7*.



	JAROSITE:	GOETHITE:	PARA-GOETHITE:	HEMATITE:
Temp (°C)	90	85	80	180 - 200
Pressure (atm O_2)				18
pH	1.3	2.5	3.6	
Acid (g/l H_2SO_4)				85
Residue Fe (%)	30	40	35	55 - 60
Residue Zn (%)	3 - 5	8 - 10	10 - 15	1
Residue Mass (t)	22.5	16.2	19.2	11.2
Overall Zn recovery (%)	97 - 98	96 - 97	94 - 95	99
Cost (CAPEX & OPEX)	Medium	Low	Low	High
Environmental	Difficult	Difficult	Difficult	Easy

FIGURE 7: COMPARISON OF COMMERCIAL IRON REMOVAL PROCESSES USED IN THE ZINC INDUSTRY TO PURIFY ZINC-RICH SOLUTIONS [DIAGRAM AFTER CLAASSEN et al., 2003; TABLE ADAPTED FROM SINCLAIR, 2005]

In recent years other technologies, such as direct leaching (at elevated temperatures and pressures) and bacterial leaching, have gained some popularity. These processes do not form zinc ferrite, so that a higher zinc recovery is achievable. New technologies may surpass the typical hydrometallurgical process in popularity. However, no matter which technology is utilised, effective iron removal is still required. The disposal of the iron residue remains a major environmental concern [Meyer *et al*., 1996]. There is a growing trend to stabilise residues, which may result in a saleable product [TU Delft, 2001].

2.2. DEFINITION OF PRECIPITATION:

Industrial crystallisation is widely used in the minerals and metals industry to generate a product, or as a means of separation or purification [Lewis, 2009].

Industrial crystallisation generally concerns the nucleation and growth of a large number of small crystals from a solution. An external action is required to induce the industrial crystallisation process. The nature of the external action determines the crystallisation method. Crystallisation methods include melt crystallisation, cooling crystallisation, evaporative crystallisation, anti-solvent crystallisation and precipitation. *Table 1* summarises the characteristics of each of the different crystallisation methods [Lewis, 2009].

This work focuses particularly on precipitation. Precipitation processes have the following characteristics:

- The chemical reaction is induced by the addition of reagents;
- The steps include nucleation, growth and secondary processes, all of which determine the final particle size distribution and precipitate product purity [Lewis, 2009; Söhnel and Garside, 1993];
- Industrial precipitation processes usually have high levels of supersaturation and fast reaction kinetics. This results in the formation of very fine particles and agglomerates with high levels of impurities. The typical particle size varies from 0.1 to 10 μm with a particle concentration of between 10^{11} and 10^{16} particles per cm^3 [Myerson, 2002]. With agglomeration growth particle size can increase to 100 μm;
- The precipitate product is sparingly soluble [Lewis, 2009; Söhnel and Garside, 1993]; and
- The precipitation process is usually the final step in a hydrometallurgical circuit, as in the case of iron removal [Habashi, 2007].

TABLE 1: A SUMMARY OF THE CHARACTERISTICS OF VARIOUS INDUSTRIAL CRYSTALLISATION METHODS [LEWIS, 2009]

CRYSTALLISATION METHOD:	PROCESS FEATURES:		PRODUCT QUALITY:	
	Solubility (wt%)	Relative supersaturation (σ)	Particle size (μm)	Purity
Melt	> 90	0.0001 to 0.01	Liquid product	Very good (after additional steps)
Cooling; Evaporative	10 to 30	0.001 to 0.01	100 - 1000 μm	Good
Precipitation; Anti-solvent	< 0.01	1 to 100	0.5 - 100 μm (agglomerates)	Poor

2.2.1. NUCLEATION:

Nucleation is the first step in the precipitation process and involves the birth of a new crystal or precipitate. Nucleation processes can be divided into the following categories [Mullin, 2001]:

- Primary nucleation occurs when the formation of a new solid phase is not influenced by the presence of the solid phase being formed. Primary nucleation can be further divided into:
  - Homogeneous nucleation occurs when the formation of the new solid phase is not initiated by the presence of any solid phase;
  - Heterogeneous nucleation is the most common in industrial processes and occurs when the formation of the new solid phase is catalysed by the presence of a foreign solid phase.
- Secondary nucleation occurs when the formation of the solid phase is initiated by the presence of the solid phase being formed; i.e. a solid phase of the same crystalline material.

The nucleation process is typically very fast, so that the size of the detectable nuclei is in the order of 10 to 100 nm [Myerson, 2002]. The formation of a critical sized cluster of molecules is required, since anything below the critical size will dissolve [Hove, 2008]. The size for a spherical cluster formed via homogeneous nucleation is given by *Equation 1*:

$$n^* = {32\pi {v_0}^2 \gamma^3}\Big/{3\Delta\mu^3} \qquad (1)$$

Where:

n^* → cluster size;

ν_0 → molecular volume (m^3);

γ → interfacial surface energy (Jm^{-2}); and

$\Delta\mu$ → net chemical potential (J).

A population of stable nuclei establishes itself in the first few minutes of a precipitation reaction, after which particle growth can commence [Söhnel and Garside, 1993]. The formation of nuclei requires that an energy barrier to nucleation be overcome [Lewis, 2009]. The work done for the formation of a nucleus of critical size is given by *Equation 2*:

$$W^* = (^1/_2)n^*\Delta\mu \qquad (2)$$

The nucleation rate is given by *Equation 3*:

$$J = zf^*C_0e^{-W^*/kT} \text{ [Becker-Döring equation, as quoted by Lewis, 2009]} \qquad (3)$$

Where:

J → the frequency of appearance of supernuclei per unit volume or area, or the net flux ($m^{-3}s^{-1}$)

z → Zeldovich factor, between 0.01 and 1; first approximation z = ½;

f^* → attachment frequency (s^{-1});

C_0 → the concentration of nucleation sites (m^{-3})

W^* → work done to form the nucleus; and

k → Boltzmann constant (1.38×10^{-23} m^2 kg s^{-2} K^{-1})

The nucleation rate is influenced by the degree of agitation, the solution density, temperature, type of neutralising agent, the presence of seed material and the level of supersaturation [Myerson, 2002]. Supersaturation is a function of pH, temperature and seed in iron precipitation. The nucleation process largely determines the number, size, structure and morphology of the precipitate particles, so that careful control should be exercised over the parameters that influence the nucleation process.

2.2.2. PARTICLE GROWTH:

Particle growth is the increase in particle size by the deposition of growth units form the mother liquor onto the particle surface, preferably in layers [Lewis, 2009]. The process occurs in two steps, namely:

- The diffusion of growth units from the bulk solution through the boundary layer toward the particle surface; and
- The integration of the growth unit into the particle surface layer at an energetically favourable site [Mersmann *et al*., as quoted by Hove, 2008].

These steps occur in the given order and either one of them may be the rate-determining step.

The overall particle growth rate, G (in m/s), is given by *Equation 4*:

$$\frac{1}{A}\frac{dm}{dt} = 6\frac{k_v}{k_a}\rho\bar{R}_{lin} \text{ (kg/m}^2\text{s)} \quad (4)$$

Where:

A → surface area of particle (m^2);

m → mass of a particle (kg);

ρ → particle density (kg/m^3);

$\bar{R}_{lin}$ → overall growth rate (m/s);

K_a → area shape factor; and

k_v → volume shape factor.

Changes in parameters such as pH, temperature, level of supersaturation, agitation, the presence of impurities, the particle population, particle shape and size all have a profound effect on the crystal growth rate [Coulson and Richardson, 2002; Söhnel and Garside, 1993].

2.2.3. SECONDARY PROCESSES – AGGLOMERATION:

Agglomeration is the dominant growth process in industrial precipitation and is defined as the size enlargement of crystals by the combination of two or more crystals to form one crystalline entity [Lewis, 2009]. The agglomeration growth process consists of three steps [Claassen, 2005]:

- Collision of particles (as a result of particle properties and the hydrodynamic environment), which is governed by the probability and frequency of collisions;
- Cohabitation of particles to allow for the formation of inter-particle bridges, which is influenced by inter-particle forces and interactions; and
- Consolidation of inter-particle bridges where nuclei, clusters and particulates are cemented together through molecular growth.

There are two types of agglomeration processes, namely:

- Perikinetic agglomeration – this type of agglomeration occurs when the collision between particles is induced by Brownian motion. Brownian motion is the random motion

of particles suspended in a fluid resulting from their collision with atoms or molecules in the surrounding solution;

- Orthokinetic agglomeration – this type of agglomeration occurs when the collision between particles is induced by shear forces [Lewis, 2009].

The overall agglomeration rate is given by *Equation 5*:

$$\frac{dm_0}{dt} = -\frac{1}{2}\beta_{aggl} m_0^2 \qquad (5)$$

Where:

m_0 → particle concentration (m^{-3}); and

β_{aggl} → agglomeration rate constant (m^3/s).

Equation 5 shows that agglomeration rate has a second order dependence on particle concentration. The agglomeration rate constant is defined by *Equation 6*:

$$\beta_{aggl} = \varphi(\dot{\gamma}, \sigma)\beta_{coll}(\dot{\gamma}) \qquad (6)$$

Where:

ψ → efficiency factor for agglomeration;

σ → relative supersaturation; and

$\dot{\gamma}$ → shear rate [Lewis, 2009].

β_{aggl} is a function of everything except particle concentration.

The parameters that have the biggest influence on the degree of agglomeration include the presence of seed, pH, temperature and the solute concentration. Other parameters that aid agglomeration include longer residence time, high diffusivity, small particles, high particle population, low viscosity, high supersaturation, agitation, additives and strong bonding forces [Lewis, 2009; Claassen, 2005].

Temperature and pH influence agglomeration through their influence on supersaturation. Temperature also influences the solution viscosity, which in turn influences the mobility and collision

frequency of particles. The surface diffusion rates of molecules increase at elevated temperatures, which supports the formation of particle bridges required for agglomeration [Claassen, 2005].

Stirring promotes agglomeration by increasing the probability of particle collision and the formation of particle bridges. However, excessive stirring can increase the collision rates to the extent that dis-agglomeration starts taking place [Claassen and Sandenbergh, 2006].

Since agglomeration is limited by the probability of particle collisions, particle population is an important parameter. It is for this reason that the presence of seed is beneficial to the agglomeration process [Claassen, 2005]. However, particle crowding is detrimental to agglomeration growth, since high collision rates and energies result in dis-agglomeration [Claassen and Sandenbergh, 2006].

The solution concentration is critical, since the solute provides the cement required to form inter-particle bridges. However, higher solution concentrations requires higher seed concentrations.
Nuclei could grow as big as 100 μm in diameter over a period of approximately 5 hours through agglomeration growth. Agglomeration growth is desirable, since it results in the formation of precipitates that have good settling, filtration and materials handling characteristics. Unfortunately, it also results in the formation of porous particles with a high surface area and high impurity content [Claassen, 2005].

2.2.4. PRECIPITATE PRODUCT QUALITY:

Precipitate product quality influences the economics of the process. The quality is defined by solids density, particle size and size distribution, settling and filtration characteristics and impurity content. The formation of large, dense particles with a uniform shape is ideal, since these particles have good dewatering characteristics and do not contain large amounts of impurities and mother liquor. The morphology and size of precipitates are determined by the nucleation, growth and secondary processes. Exercising control over these processes can aid in the formation of a good quality precipitate [Claassen, 2005].

The ideal precipitate is filterable and washable; contains minimum valuable metal, while also removing other unwanted impurities; is environmentally stable and compact, and potentially saleable [TU Delft, 2001].

In reality, industrial precipitation processes produce very fine, irregular, voluminous and amorphous precipitates that contain high levels of impurities and result in the loss of valuable metals. Dewatering and materials handling of these precipitates is challenging and expensive.

2.3. KEY PARAMETERS TO CONSIDER IN PRECIPITATION:

2.3.1. TEMPERATURE AND pH:

An increase in temperature improves the efficiency of the precipitation reaction. Haegele *et al* (1992a) found that the precipitation efficiency increased from 75 % at 60 ^{o}C to over 90 % at 75 ^{o}C.

IMPACT ON THERMODYNAMICS:

Temperature and pH determine the thermodynamic stability of iron phases at a particular solution concentration and supersaturation level. This is illustrated in the stability diagram in *Figure 6*, and the metastable zone graph in *Figure 8*. Precipitates could re-dissolve outside of the pH range where precipitation occurred. An increase in temperature increases the solubility of the precipitate at a particular pH [Habashi, 2007].

IMPACT ON KINETICS:

These parameters also have an impact on the kinetics of the iron precipitation reaction through their influence on supersaturation, which is the driving force for precipitation. An increase in operating temperature often leads to an increase in the rate of nucleation, growth and secondary processes, such as agglomeration [Söhnel and Garside, 1993]. Wang *et al*., 1985 (as quoted by Claassen, 2002) attempted to describe the kinetics of iron removal as an alkali-Jarosite. They found that the rate of iron removal increases dramatically with an increase in temperature.

An increase in the reaction rates result in a decrease in the required residence time. Claassen, 2002 confirmed this when he showed that an increase in operating temperature could decrease the required retention time for nucleation and growth.

IMPACT ON PRECIPITATE QUALITY:

Supersaturation determines the precipitate quality in terms of crystal size, shape, mineralogical phase and stability. These particle properties determine the moisture content of the cake, which determines the dissolved zinc loss [Claassen, 2005]. Temperature and pH influence precipitate quality through their influence on supersaturation.

An increase in pH and temperature results in elevated supersaturation levels and a high rate of diffusion of iron species to the growth points. These conditions lead to the entrainment of unleached neutralising agent and zinc sulphate solution, which determines the undissolved zinc losses through the precipitate [Sakamoto et al., 1976 and Yamada, 1980 as quoted by Claassen, 2005]. High pH levels also reduces the reactivity of the neutralising agent, exacerbating the problem [Claassen, 2005].

2.3.2. SUPERSATURATION:

DEFINITION:

A saturated solution is one that is in thermodynamic equilibrium with the solid phase of its solute at a given temperature. A supersaturated solution is one that contains more of the dissolved solute than that given by the equilibrium saturation value [Coulson and Richardson, 2002]. Supersaturation is the driving force for industrial precipitation processes.

THE METASTABLE ZONE:

The metastable zone is the region between the solubility curve and the metastability limit and indicates the ideal operating parameters to generate the best quality precipitate. *Figure 8* illustrates work done by Claassen to define the boundaries of the metastable zone as a function of pH and temperature.

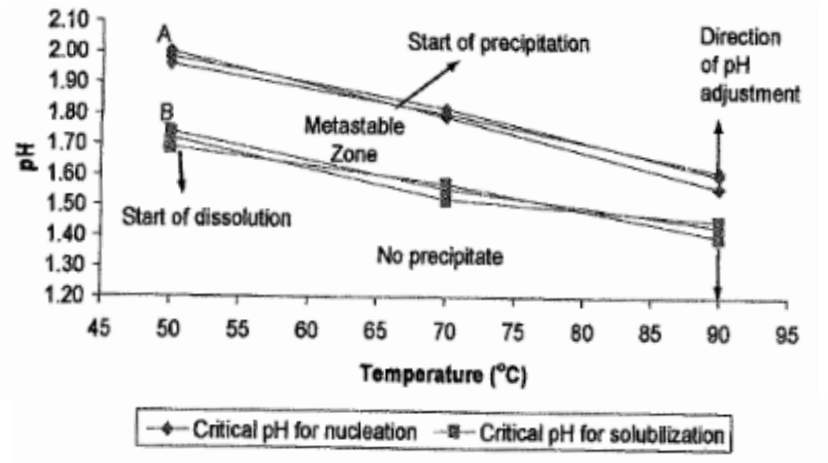


FIGURE 8: THE METASTABLE ZONE FOR THE PRECIPITATION OF IRON FROM A FERRIC SOLUTION CONTAINING 11.5 g/l Fe AS $Fe_2(SO_4)_3$ AND 5 g/l H_2SO_4. NEUTRALISATION WAS DONE WITH $Ca(OH)_2$ AND ZnO POWDER; THE ACID WASH WAS DONE WITH 98% H_2SO_4 [CLAASSEN, 2005]

Supersaturation within the metastable zone is low, so that particle growth is favoured and large, dense particles of a uniform size are formed. Coarse and well-defined particles are typically formed from dilute solutions [Söhnel and Garside, 1993]. However, the metastable zone is very narrow and requires precise control of operating conditions. Most industrial iron removal processes operate above the metastable zone where high supersaturation levels are prevalent. When operating the iron removal process within this area the formation of very fine and amorphous precipitate is common. Agglomeration growth, however, is favoured within this zone. While agglomerated particles are large in diameter and have good dewatering characteristics, they are porous, have a large surface area and high levels of impurities [Claassen, 2005; Claassen and Sandenbergh, 2006].

The metastable zone highlights the fact that the formation of good quality precipitates requires control of the supersaturation level. The level of supersaturation is controlled through the careful selection of parameters, such as pH and temperature. The width of the metastable zone can be reduced with increasing temperature, increased mixing intensity and the presence of seed [Claassen, 2005].

2.3.3. SEED:

THE IMPACT ON REACTION KINETICS:

The presence of seed impacts on nucleation by reducing the width of the metastable zone [Coulson and Richardson, 2002]. The presence of seed can significantly enhance an operation by promoting both the nucleation and growth processes [Sinclair, 2005]. The particle growth rate is dependent on the number of seed particles present, the seed size and surface area.

Seeding with recycled solids has been found to have a catalytic effect on the rate of oxidation for iron [Hove, 2008]. Jarosite precipitation is dependent on the presence of seed, with even a small amount of seed greatly increasing the rate of the precipitation reaction. The rate increase is almost linear with an increase in seed addition. This was confirmed by Wang *et al* (1985) (as quoted by Claassen, 2002). The authors attempted to describe the kinetics of iron removal as an alkali-Jarosite and found that the presence of seed shortens the residence time required for iron removal by several hours. This is because seed eliminates the incubation time required to form a new phase. The precipitation rates are highest with recycled solids, probably as a result of lattice compatibility [TU Delft, 2001].

THE IMPACT ON UNDISSOLVED ZINC LOSSES:

Only between 10 and 20 % of the insoluble zinc losses through the iron residue are attributed to the presence of insoluble zinc ferrite in the calcine. The remainder of the losses can be attributed to the encapsulation of unleached neutralising agent with iron precipitate [Claassen *et al.*, 2003].

Seed provides additional surface area for precipitation to take place. Additionally, lower activation energy is required for precipitation onto isomorphic surfaces, so that iron precipitates preferentially onto the surface of seed material, rather than neutralising agent. In the presence of seed there are fewer instances of coating of unleached neutralising agent. This was confirmed by Claassen (2005), when he demonstrated that the presence of seed improves precipitate purity and results in a decrease in the undissolved zinc losses.

THE IMPACT ON DISSOLVED ZINC LOSSES:

Very few new nuclei are formed in the presence of seed, because atoms are layered onto existing surfaces of the seed particles. The presence of other particles in a reactor may promote particle or agglomeration growth and lead to an increase in the final particle size [Söhnel and Garside, 1993].

An increase in final particle size results in a precipitate product with good settling and filtration characteristics. Filterability is a measure of the dissolved zinc losses. Claassen (2005), found that the presence of even a small amount of seed improves the filterability of the precipitate by up to 80 %. He attributed the improvement to a reduction in the number of particles, an increase in the overall particle size of the precipitate and a decrease in the surface area. Hove (2008) showed an improvement in settling rates in the presence of seed. He found that seeding improves the dewatering characteristics of the precipitate, probably due to increased size and density of the precipitate.

2.3.4. NEUTRALISING AGENT:

THE IMPACT ON UNDISSOLVED ZINC LOSSES:

The use of a zinc-rich neutralising agent contributes to the high insoluble zinc losses prevalent in most commercial iron removal technologies. The critical factors to consider when selecting a potential neutralising agent is the zinc content, the particle size and the reactivity or utilisation efficiency. Particle size effects the utilisation efficiency as well as the probability of coating. Coarse neutralising agents do not have sufficient time to leach completely before being coated by precipitate product.

Claassen (2002), showed that the use of an alternative neutralising agent that contains no zinc, such as slaked lime or limestone, is one way to limit the insoluble zinc losses associated with the use of zinc-rich neutralising agents in traditional iron removal processes.

SLAKED LIME AS A NEUTRALISING AGENT:

Slaked lime is used in the hematite process to neutralise excess acidity in the process solution before iron removal, as well as to aid iron and silica removal before the solvent extraction of zinc. The use of slaked lime was attempted at Zincor some years ago, but was stopped when very poor settling and filtration was experienced. The poor settling was probably due to a lack of seed. Claassen's work showed that the use of slaked lime for neutralisation resulted in high zinc losses as a result of the entrainment of zinc-rich solution in the precipitate. This finding confirms the poor settling and filtration observed during the plant trial.

CHEMICALLY PRECIPITATED LIMESTONE AS A NEUTRALISING AGENT:

Chemically precipitated limestone is produced as a waste product in the paper and pulp industry. It is cheaper than slaked lime and has a high utilisation efficiency, due to the small average particle size. During Claassen's work, this neutralising agent performed the best in terms of zinc recovery.

However, the one disadvantage of using calcium-based neutralising agents (like slaked lime or chemically precipitated limestone) is the large volume of residue generated. This is because the neutralisation reaction generates gypsum. The volume is almost double that of a typical iron residue.

BASIC ZINC SULPHATE AS A NEUTRALISING AGENT:

Claassen also investigated the use of Basic Zinc Sulphate, which is the cake from the magnesium bleed. The gypsum present in the cake acts as a filter aid. While most of the zinc contained in the cake is leached, some coating by iron precipitate can occur, resulting in insoluble zinc losses. Claassen combined this product with zinc oxide for neutralisation and found a decrease in the insoluble zinc losses. The reason was attributed to the higher reactivity of the combination of these neutralising agents compared to calcine.

A more recent plant trial done at Zincor in 2010, supplemented the combination of DRC oxide and calcine with Basic Zinc Sulphate. While this work was not able to quantify the effect on the zinc losses, there was a noticeable improvement in the filterability of the residue [Majeke, 2010]. The improvement was attributed to the gypsum present in the Basic Zinc Sulphate cake, which acts as a filtration aid. A similar improvement had been observed in the filtration on the Pb/Ag belt with the

addition of Basic Zinc Sulphate into the HAL and SHAL stages. Since there was a practical limitation on the bleed rate, one would have to decrease or cease addition into the HAL stage in order to be in a position to add Basic Zinc Sulphate into the Iron Removal Stage. This would have compromised the soluble zinc loss through the Pb/Ag residue.

Swarnkar *et al.* (1995), also successfully used Basic Zinc Sulphate from a magnesium bleed plant to neutralise acid and control iron in a leach solution to acceptable levels.

In summary, the use of a more reactive neutralising agent or one that contains little or no zinc, could potentially reduce the zinc losses through the iron residue.

2.3.5. RESIDENCE TIME:

Residence time is the average amount of time that a particle spends within a particular system. Residence time begins from the moment a particle enters the system until the moment that it exits.

It is generally accepted that the average particle size increases as the mean residence time is increased [Söhnel and Garside, 1993]. Longer residence time promotes agglomeration, so that an increase in residence time results in an increase in the final particle size [Lewis, 2009; Claassen, 2005]. Haegele *et al*. (1992a) found that an increase in residence time improves the quality of the residue.

2.3.6. SOLUTION CONCENTRATION:

The solute supplies the cement needed to form inter-particle bridges during crystal growth. Claassen and Sandenbergh (2006) found that an increase in the solution concentration could result in the formation of bigger particles. However, one needs to accommodate for the increase by increasing the addition of seed.

Supersaturation levels are high above the metastable zone where most industrial precipitation processes operate (as seen in *Figure 8*). When in this zone, a further increase in solution concentration will result in an increase in supersaturation levels. For the influence of supersaturation on soluble and insoluble zinc losses see *Section 2.3.2.*

2.3.7. VISCOSITY:

Solution viscosity describes the internal friction of a moving fluid, or it is a measure of a solution's resistance to flow. Solution viscosity is a function of pressure, temperature and solute concentration [Themelis, 1995]. The viscosity of a solution increases with an increase in solute concentration and decreases with an increase in temperature.

Thickening and filtration are common dewatering practices used in hydrometallurgical processes. Thickening requires particles to have good settling characteristics, which is very much influenced by the viscosity of the solution. In fact, solution viscosity is the most important parameter affecting settling rates in a thickener [Majeke, 2010]. High solution viscosity restricts the ease at which particles can move in the liquor. It is for this reason that dilution of the thickener feed is often recommended to improve settling rates.

2.3.8. HYDRODYNAMIC CONDITIONS:

Since precipitation involves the movement of solid particles within a liquor, the hydrodynamic environment within a reactor plays an important role. Hydrodynamic conditions are determined by reagent addition points, baffles, agitator design and stirring speed. Changes in these conditions impact particle growth and agglomeration by influencing the probability of particle collisions and the formation of inter-particle bridges [Seyssiecq *et al*, 1998 as quoted by Claassen 2005].

THE EFFECT OF MIXING:

Three stages of mixing exist, namely macromixing, mesomixing and micromixing. Macromixing occurs on the scale of the reactor diameter, while micromixing occurs on a molecular level. Since the chemical reaction, nucleation, crystal growth and secondary processes all occur on a molecular level, the role of micromixing is critical in precipitation. This was confirmed by Claassen and Sandenbergh (2007).

The boundary layer is a stagnant layer of solution surrounding the particle through which particles from the mother liquor have to diffuse to reach the crystal surface. The particle growth rate increases with a decrease in the width of the boundary layer. The width of the boundary layer is decreased by increasing the stirring intensity. Increasing the stirring speed beyond a certain maximum will disrupt particle growth and cause dis-agglomeration [Söhnel and Garside, 1993].

The ideal stirring intensity promotes the formation of more uniform particles and reduces the required residence time by decreasing the induction period [Coulson and Richardson, 2002]. The induction period is the time between initiating the precipitation reaction and the appearance of the first precipitate. An increase in stirring intensity can decrease the induction period up to a certain critical stirring speed, after which a further increase will have no benefit.

THE EFFECT OF THE REAGENT ADDITION POINT:

Claassen and Sandenbergh (2006) found that effective mixing of the reagent streams with the bulk solution is essential to minimise high local supersaturation and ensure the formation of good quality precipitate. This is achieved when the feed points are placed on opposite sides of the reactor, near the agitator blades with the inlets just below the solution surface.

2.3.9. SUMMARY:

KEY PARAMETERS THAT INFLUENCE DISSOLVED ZINC LOSSES:

The zinc contained in the cake moisture is known as soluble zinc loss. *Figure 9* summarises the parameters that have the biggest impact on the soluble zinc losses through the Fe residue. They include the filterability of the precipitate, the washing efficiency and the condition of the filtration equipment.

FILTERABILITY:

The filterability of the precipitate is a good indication of what the soluble zinc loss will be. Filterability depends largely on the physical characteristics of the precipitate and the liquor.

The physical characteristics of the precipitate include density, size and size distribution. Large, dense particles tend to have good dewatering characteristics. The physical characteristics are a function of pH, temperature, supersaturation, seeding, residence time and hydrodynamic conditions. Long residence time, the presence of seed and adequate mixing all promote particle growth.

The physical characteristics of the solution include the density and viscosity and impact on particle settling. High density and viscosity hinder particle settling.

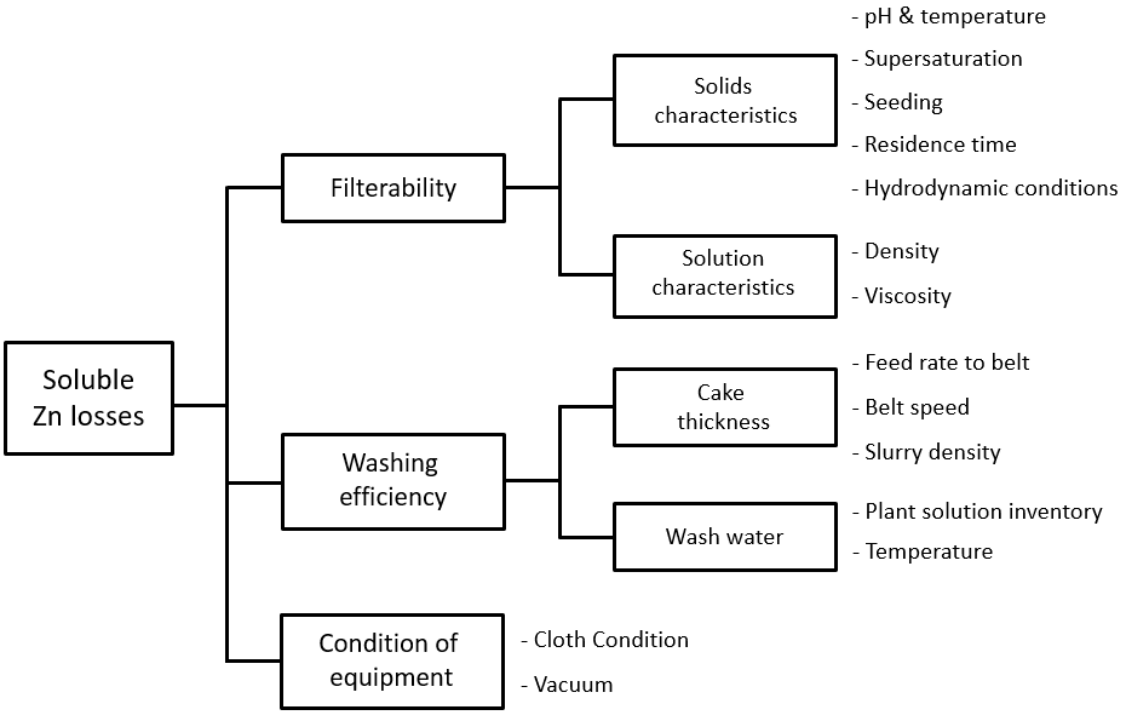


FIGURE 9: SCHEMATIC OF THE PARAMETERS THAT INFLUENCE THE SOLUBLE ZINC LOSSES THROUGH THE FE RESIDUE

WASHING EFFICIENCY:

Wash ratio is the mass of wash water divided by the mass of residue. Increasing the wash ratio (up to a certain maximum) is almost guaranteed to reduce the soluble zinc losses if the precipitate has good dewatering characteristics. Wash water addition is limited by the plant solution inventory. Hot wash water results in a better zinc recovery from the cake [Haegele *et al*., 1992a]. Haegele *et al*., 1992b found that between 50 and 70 % of zinc contained in entrained solution in unwashed precipitate can be recovered by washing. The cake thickness, belt speed and available filter area all play an important role in washing efficiency.

CONDITION OF PROCESS EQUIPMENT:

The process equipment needs to be well maintained and in good condition to ensure good filtration. The filter cloth, spray nozzles, slurry distribution system and vacuum pumps are especially critical.

SUMMARY:

Careful control of key parameters should make it theoretically possible to maintain the soluble zinc loss below 0.5 %. This was achieved for seven months during the period of 1 January 2009 to 30 September 2011.

KEY PARAMETERS THAT INFLUENCE UNDISSOLVED ZINC LOSSES:

Figure 10 is a schematic summary of the parameters that most impact the insoluble zinc losses through the Fe residue. They include the neutralising agent and HIS quality, as well as the process parameters.

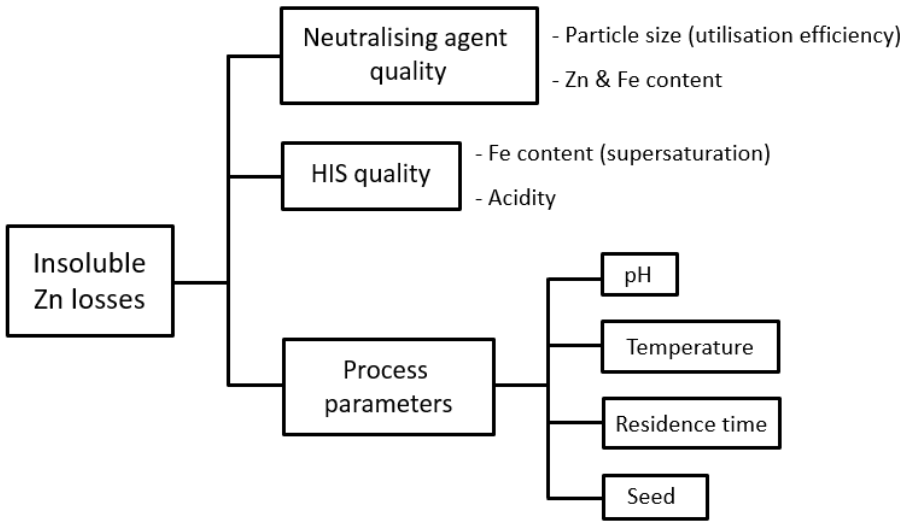


FIGURE 10: SCHEMATIC OF THE PARAMETERS THAT INFLUENCE THE INSOLUBLE ZINC LOSSES THROUGH THE FE RESIDUE

NEUTRALISING AGENT QUALITY:

Zinc ferrite, or Franklinite ($ZnFe_2O_4$), is formed during concentrate roasting. It is insoluble at the operating conditions maintained in the Iron Removal Stage, so that the zinc contained in the zinc ferrite reports to the residue as an insoluble zinc loss.

Coating of the neutralising agent by iron precipitate also occurs. When using a zinc-rich neutralising agent, this zinc reports to the residue as an insoluble zinc loss. Particle size plays an important role in the utilisation efficiency of neutralising agents. Smaller particles have a larger available surface area and dissolve more readily, so that there is less opportunity for coating to occur.

The ideal neutralising agent is one that contains little or no zinc, has a high utilisation efficiency and is cheap and readily available.

SOLUTION QUALITY:

When operating above the metastable zone, an increase in the iron content increases the level of supersaturation. High levels of supersaturation result in the formation of very fine and amorphous particles that are difficult and expensive to treat downstream.

PROCESS PARAMETERS:

pH and temperature are key parameters, since they determine the iron phase formed and impact on the degree of supersaturation. Temperature increases the rate and efficiency of precipitation.

Seeding promotes agglomeration growth and provides additional surface area for iron to precipitate onto, thereby decreasing both the soluble and insoluble zinc losses. Seeding cannot be implemented at the expense of residence time, since residence time is essential for particle growth.

SUMMARY:

The precipitate quality and iron removal efficiency are most sensitive to pH, followed by seed, temperature and HIS concentration [Claassen, 2005]. Careful control of these parameters within the ideal operating window should make it possible to consistently maintain the insoluble zinc loss below 1.25 %. This was achieved for five months during the period of 1 January 2009 to 30 September 2011.

2.4. FORMULATION OF RESEARCH AIMS AND HYPOTHESIS:

The insoluble zinc loss through the iron residue was the second biggest contributor to the overall zinc losses. The insoluble zinc loss was attributed to the presence of zinc ferrite in the neutralising agent, as well as the coating of zinc-rich neutralising agent by iron precipitate. The soluble zinc loss was related to the dewatering characteristics of the iron precipitate.

A review of literature showed that the use of alternative neutralising agents (containing little or no zinc) to supplement or replace calcine, could potentially reduce the insoluble portion of the zinc loss.

The study also showed that seed provides additional surface area for precipitation so that less coating of zinc-rich neutralising agent occurs, thereby reducing the insoluble zinc loss. Seed also promotes agglomeration growth and the formation of a precipitate with good settling and filtration characteristics, thereby reducing the soluble zinc loss.

Due to the limitations of the experimental procedure (which will be elaborated on in *Section 3.1.2* and *4.1.2*), the outcome of this work was not conclusive. Instead, the tentative conclusions drawn would support a further in-depth study.

3. LABORATORY WORK:

3.1. METHODOLOGY:

3.1.1. SCOPE OF WORK:

The laboratory work evaluated calcine and DRC oxide, as well as alternative neutralising agents, in combination with a seed recycle, in an attempt to reduce the zinc losses through the iron residue.

This portion of the experimental work consisted of three parts, namely:

- Preliminary laboratory work to establish an experimental procedure that closely resembled the plant set-up, as well as a preliminary evaluation of the presence of seed ;
- Preliminary laboratory work to identify potential alternative neutralising agents to supplement or replace calcine; and
- Final laboratory work to evaluate the chosen alternative neutralising agents, together with a seed recycle.

3.1.2. LIMITATIONS:

Each experimental scenario was only evaluated once, so that the results obtained were not considered statistically significant or conclusive. However, observations could be made and tentative conclusions drawn, in order to support further work.

3.1.3. GENERAL EXPERIMENTAL SET-UP:

A schematic of the experimental set-up, also indicating the sampling points, can be seen in *Figure 11*. A picture of the actual set-up is shown in *Figure 12.* Every attempt was made to simulate typical plant conditions. The set-up consisted of six 3-litre polypropylene reactors in series on a cascading stand. Each reactor had baffles with an overflow pipe. A rubber hose was attached to the end of each overflow pipe and extended into the next reactor to simulate a down pipe to prevent short-circuiting. Double-bladed agitators, similar to those used in the Zincor operation, were made up.

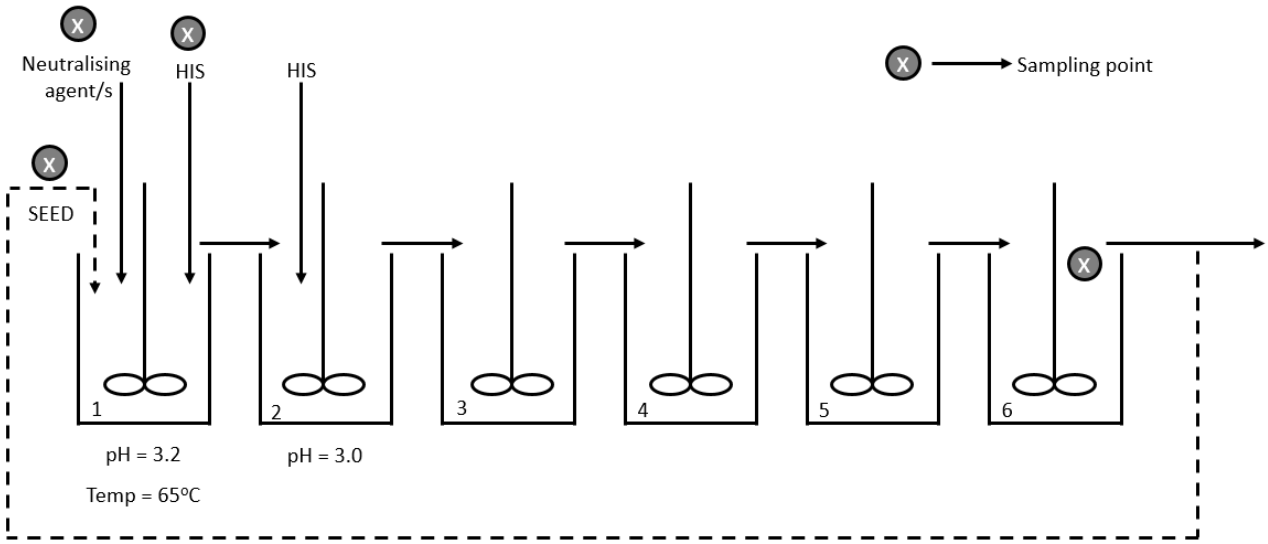


FIGURE 11: EXPERIMENTAL SET-UP INDICATING THE SAMPLE POINTS AND THE SEED RECYCLE

Hot water baths were used to heat the feed solutions and maintain them at temperature. Hot water was circulated from the hot water bath through sealed coils to maintain the temperature in each of the reactors. The water baths had to be topped up at regular intervals, due to water loss through evaporation. Each reactor was covered with a Perspex lid to preserve heat and prevent loss of water through evaporation. *Figure 13* shows a close-up view, as well as a schematic, of one of the reactors with Perspex lid, double-bladed agitator, baffles, heating coil, 'down' pipe and overflow pipe.

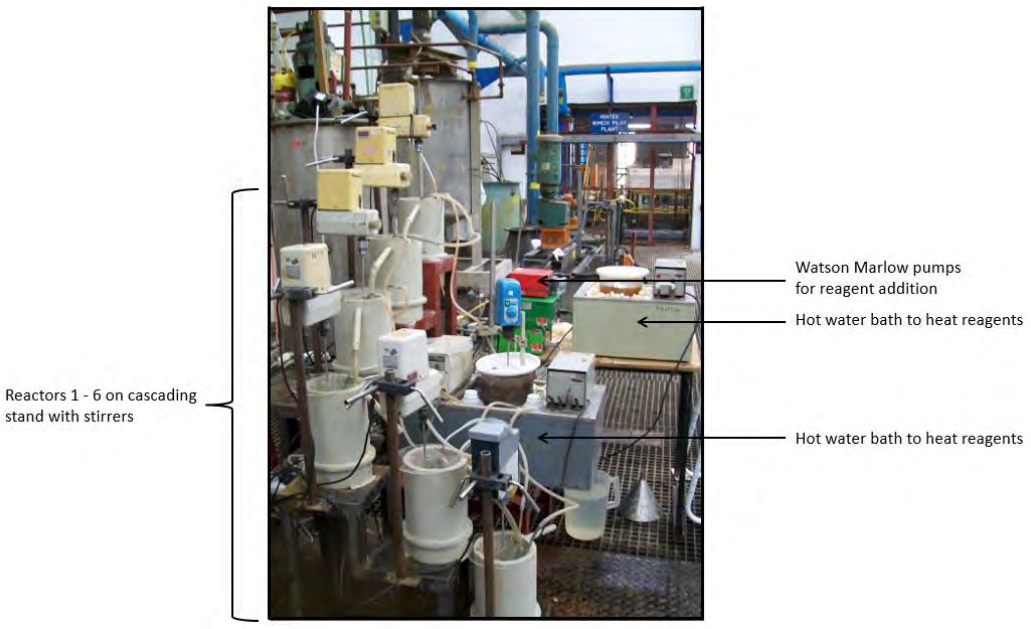


FIGURE 12: ACTUAL LABORATORY SET-UP

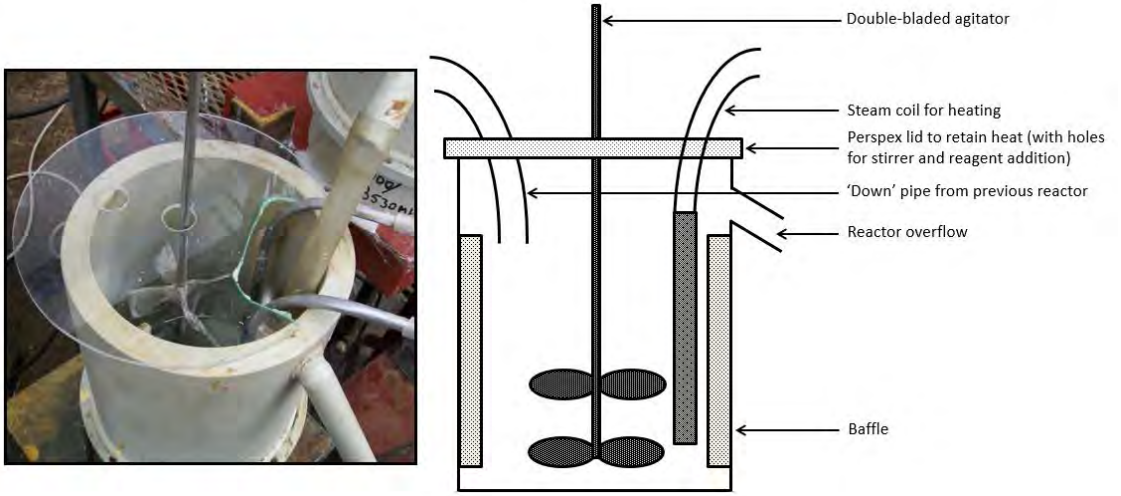


FIGURE 13: REACTOR WITH BAFFLES, PERSPEX LID, STIRRER, STEAM COIL, 'DOWN' PIPE AND OVERFLOW PIPE

3.1.4. GENERAL EXPERIMENTAL PROCEDURE:

The temperature was maintained at 65 ^{o}C through manual adjustment. The temperature was fairly constant and varied from the set-point by $\pm$ 1 ^{o}C. The stirring speed was 150 rpm throughout, which was sufficient to keep the solids in suspension, but not vigorous enough to result in splashing.

The iron was removed from the HIS through a hydrolysis reaction. This was achieved through the addition of neutralising agent/s into the first reactor to maintain a pH of 3.2. The acid wash in the second reactor was achieved by adding a small amount of HIS to reduce the pH to 3. The flowrate of the HIS was kept constant, while that of the neutralising agent/s was adjusted slightly to maintain the pH profile at the desired set-point.

The typical residence time in the Zincor operation was approximately one hour per reactor. To maintain the same residence time in the laboratory a total flow of 50 ml/min was required. Depending on the type of neutralising agent being added and whether a seed recycle was being evaluated, the HIS flowrate was approximately 40 ml/min, with the flowrate of the other streams making up the difference of 10 ml/min. The reagents were added continuously with Watson Marlow peristaltic pumps, with the reagent addition points just beneath the agitator blades on opposite sides of the reactor [Claassen and Sandenbergh, 2007a]. The Watson Marlow pumps were also used for the seed addition. A 50 % volume recycle was achieved from the final reactor back into the first reactor.

3.1.5. FEED MATERIALS, SAMPLING & ANALYSES:

Actual plant materials (solutions and solids) were used in all the laboratory experiments. Sampling was done on an average day to ensure that the samples were representative of typical plant conditions. Sufficient sample was taken of each of the streams to use throughout the laboratory work.

The HIS sample was stored in a 250 litre drum. The liquor was stirred thoroughly before decanting sufficient sample for each experimental run. The samples were filtered to remove any gypsum that had precipitated and settled during cooling.

All slurry samples were stored in large buckets. The slurry was mechanically stirred before decanting a sufficient amount for each experiment. The slurry was screened to remove coarse grit.

Each feed stream was sampled at the start of every experiment and a final slurry sample was taken on completion. The size of the samples depended on the analyses required. Each portion of the laboratory work required different analyses, which will be elaborated on in *Sections 3.1.7* and *3.1.8*.

All flowrates, volumes, densities and masses were recorded for the purposes of completing a thorough mass balance.

3.1.6. MASS BALANCE:

A mass balance was performed for each experiment to determine the zinc recovery, soluble and insoluble zinc losses. The schematic in *Figure 14* demonstrates the principles used in the mass balance.

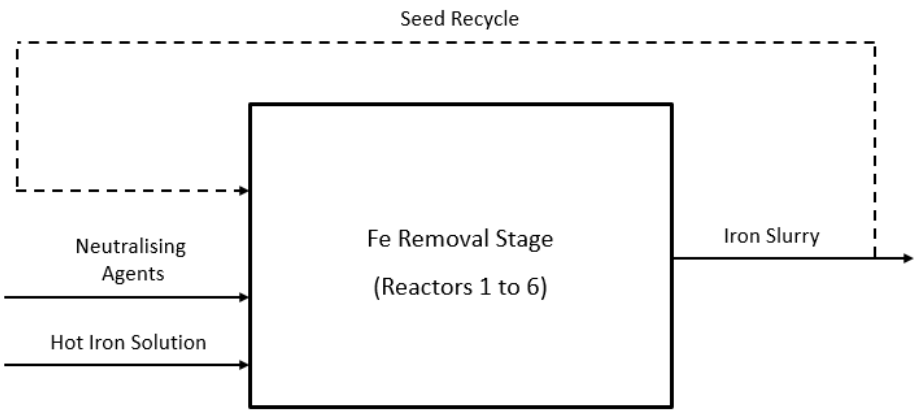


FIGURE 14: SCHEMATIC INDICATING THE INPUT AND EXIT STREAMS WITH THE SEED RECYCLE FOR THE MASS BALANCE

The zinc balance was performed according to *Equation 7*:

$$Zn_{IN} = Zn_{OUT}$$

$$Zn_{Neutralising\ Agents} + Zn_{HIS\ (for\ Rectors\ 1\ and\ 2)} + Zn_{seed\ recycle} = Zn_{Fe\ Slurry} + Zn_{seed\ recycle}$$

$$Zn_{Neutralising\ Agents} + Zn_{HIS\ (for\ Rectors\ 1\ and\ 2)} = Zn_{Fe\ Slurry} \quad (7)$$

Only the zinc in the incoming and exit streams were accounted for, while the zinc contained in the seed was ignored.

No mass balance is without inaccuracies, so that there will always be an 'unaccounted' loss. The unaccounted portion is usually attributed to the stream that is most difficult to measure accurately. In this case, the unaccounted loss was likely due to inaccuracies in measuring the neutralising agent stream. A slurry is notoriously difficult to account for accurately, due to its two-phase nature. Added to this, the flow of this stream was adjusted occasionally to maintain the pH profile, making the exact volume added over the duration of the experiment difficult to determine. Since the unaccounted portion was attributed to an input stream, it was calculated by taking the zinc in the output stream and subtracting from it the zinc in the input streams.

3.1.7. PRELIMINARY LABORATORY WORK:

3.1.7.1. DETERMINING EXPERIMENTAL PROCEDURE & EVALUATION OF SEEDING:

The purpose of this portion of the experimental work was to develop an experimental procedure that closely represented the plant conditions, as well as evaluate the impact of seed.

The experimental set-up shown in *Figure 11* was used, except that the acid wash step in the second reactor was not performed and there was no seed recycle. Only calcine was used as a neutralising agent, since the purpose of this work was not to evaluate the merits of alternative neutralising agents. A summary of the experimental program and parameters is given in *Table 2*.

The first experiment was started with empty reactors. The HIS flow was kept constant, while the calcine slurry flow was adjusted to maintain the pH in the first reactor at 3.2. The temperature was manually controlled at 65 ^{o}C ($\pm$ 1 ^{o}C) across all six reactors. The experiment was stopped once the final reactor was on overflow. A 500 ml slurry sample was taken from the final reactor. The sample was filtered and the cake was washed. The filtrate SG was recorded and a sample was sent for Zn analysis.

The thickness and mass of the filter cake were recorded, before sealing and submitting the sample for chemical analyses to determine cake moisture, soluble and insoluble Zn content. A small slurry sample was also taken from each of the six reactors and sent for particle size distribution analyses using a Malvern Particle Size Analyser. Once sampling had been completed, the hot water baths and stirrers were switched off and the slurry was left to cool.

TABLE 2: A SUMMARY OF THE EXPERIMENTS AND OPERATING PARAMETERS

No.	Temp (°C)	pH	Residence time per reactor (min)	'SEED'
1	65	3.2	69	No
2	65	3.2	68	Yes
3	65	3.2	68	Yes
4	65	3.2	51	Yes
5	65	3.2	52	Yes

The next morning all the stirrers and heaters were switched on and the feed streams were heated in the hot water baths. The heating coils were used to heat the slurry, or 'seed', from the first experiment. The feed was started up again once all the feed streams and reactors had reached the desired temperature of 65 °C. As before, the HIS flowrate was kept constant, with only the calcine slurry flowrate being adjusted slightly to maintain a pH of 3.2 in the first reactor. The experiment ran for an equivalent of six reactor volumes before being terminated. The residence time was approximately 1 hour per reactor, or 6 hours for the whole set-up. As before, a 500 ml slurry sample was taken from the final reactor and small slurry samples were taken from each of the reactors to determine the particle size distribution. The stirrers and heaters were switched off once the necessary samples had been taken. The contents in the reactors were left to cool to be used as 'seed' for the next experiment. This procedure was repeated another three times (refer to *Table 2*).

3.1.7.2. IDENTIFYING ALTERNATIVE NEUTRALISING AGENTS:

This portion of the work evaluated a number of alternative neutralising agents as supplements or replacements for calcine. The alternative neutralising agents to be evaluated included the following:

- DRC oxide, which was already in use on the plant as a supplement to calcine.
- Effluent Treatment Plant (ETP) thickener underflow, which consisted mostly of zinc, gypsum and a number of impurities. The gypsum would provide seed and potentially aid filtration. A potential upside would be the recovery of some of the Basic Zinc Sulphate contained in this residue stream. The zinc content was approximately 12 %.

- Basic Zinc Sulphate (BZS), which was a re-pulped cake from the Magnesium Bleed Plant and contained mostly zinc and gypsum. The BZS was already being added into the HAL stage where the gypsum acted as a filter aid on the Pb/Ag belt. The majority of the 12 % zinc contained in this cake would be recovered.
- Slaked lime and chemically precipitated $CaCO_3$ (which will be referred to as limestone), which were already being used as neutralising agents in the Magnesium Bleed Plant and the Effluent Treatment Plant. These neutralising agents contained no zinc or iron that could contribute to high insoluble zinc losses, either through coating or the presence of zinc ferrite.
- Bag house dust and brown ash, which were zinc oxide by-products from the smelting operation. Since these products were sold at discounted prices to small zinc operators, it would be to Zincor's advantage to retreat the material instead. This material had a zinc content of approximately 80 % and very little or no iron. The lack of iron meant that the presence of zinc ferrite would be minimal. There was still a risk of zinc loss through coating of the neutralising agent with iron precipitate.

TABLE 3: CHEMICAL AND PSD ANALYSES OF THE ALTERNATIVE NEUTRALISING AGENTS

ANALYSES:	DRC Oxides	ETP U/F	Basic Zinc Sulphate	Lime	Limestone	Bag House & Brown Ash
Zn (%)	70.11	12.70	12.79			83.45
Fe (%)	0.78	1.53	0.13			0.11
Ca (%)	0.18	16.21	19.68	49.57	37.52	
SiO_2 (%)				1.00	0.72	
F (%)	0.04					0.00
Cl (%)						0.25
Cu (%)		0.22				
Cd (%)		0.06				
Pb (%)		0.20				
Co (%)		0.13				
Mn (%)		2.50	0.62			
Mg (%)		2.42	0.09			
Slurry density	1.14	1.05	1.22	1.08	1.07	1.24
Slurry solids (%)	28.00	15.79	27.60	19.52	2.77	25.69
D50 (µm)	0.23	6.64	20.12	5.00	6.80	24.15

Table 3 compares the chemical analyses and particle size of the various alternative neutralising agents. DRC oxide was the finest. The bag house and brown ash mixture had the largest particle size, likely due to the presence of fine metallic zinc in the brown ash dross. These two neutralising agents also had the highest zinc content. The ETP thickener underflow and Basic Zinc Sulphate both contained a number of other impurities, which would potentially re-dissolve under the experimental conditions.

The purpose of this portion of the work was to evaluate each of the potential neutralising agents. The precipitation step would be sufficient to do this assessment and narrow the selection down to at least two alternatives for further study. The schematic of the laboratory set-up is shown in *Figure 15*.

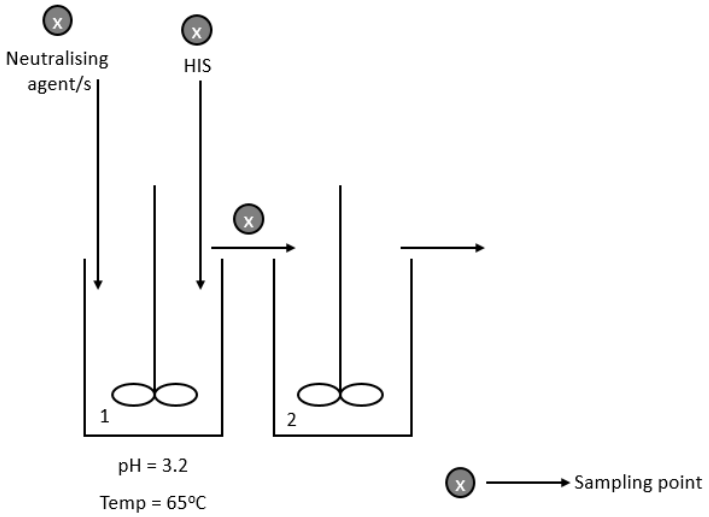


FIGURE 15: SCHEMATIC OF THE LABORATORY SET-UP USED TO EVALUATE ALTERNATIVE NEUTRALISING AGENTS, ALSO INDICATING SAMPLE POINTS

Seed was generated using calcine. Chemical analysis was done on the seed and considered for the purpose on the mass balance. The slurry, together with the HIS and neutralising agents, were pre-heated to 65 °C in the hot water bath.

The experiment was run across two reactors with the first reactor containing 2.5 litres of seed at commencement of the experiment. The HIS and respective neutralising agent were added into the first reactor at a total flowrate of approximately 50 ml/min to give a residence time of approximately 1 hour per reactor. The HIS flow was kept constant and the flowrate of the neutralising agent was adjusted to maintain the pH at 3.2. The experiment was terminated once the second reactor was on overflow.

A 500 ml slurry sample was taken from the first reactor, while the contents of the second reactor was discarded. The slurry sample was filtered and washed. The filtrate SG was recorded and the filtrate sample sent for chemical analyses. The wet cake thickness and mass were recorded and the cake sent for chemical analyses. *Table 4* details the analyses done on the samples for each of the experiments. ICP (Inductively Coupled Plasma) was used to determine the chemical compositions.

TABLE 4: A SUMMARY OF THE ANALYSES PERFORMED ON THE PRECIPITATE GENERATED THROUGH NEUTRALISATION WITH VARIOUS ALTERNATIVE NEUTRALISING AGENTS

EXPERIMENTS:	SAMPLES:	SOLIDS ANALYSES (%):	SOLUTION ANALYSES (g/l):
DRC oxides	Seed	Zn	Zn
	HIS	No solids	Zn
	Oxide Slurry	Zn & F	None (water)
	Iron Residue	Zn & F	Zn & F
ETP U/F	Seed	Zn	Zn
	HIS	No solids	Zn, Mn & Mg
	ETP Slurry	Zn, Mn & Mg	None (treated water)
	Iron Residue	Zn, Mn & Mg	Zn, Mn & Mg
Basic Zn Sulphate	Seed	Zn	Zn
	HIS	No solids	Zn, Mn & Mg
	BSZ slurry	Zn, Mn & Mg	None (treated water)
	Iron Residue	Zn, Mn & Mg	Zn, Mn & Mg
Lime	Seed	Zn	Zn
	HIS	No solids	Zn, Ca & SiO_2
	Lime Slurry	Ca & SiO_2	None (water)
	Iron Residue	Zn, Ca & SiO_2	Zn, Ca & SiO_2
Limestone	Seed	Zn	Zn
	HIS	No solids	Zn, Ca & SiO_2
	Limestone Slurry	Ca & SiO_2	None (water)
	Iron Residue	Zn, Ca & SiO_2	Zn, Ca & SiO_2
Bag House dust & Brown Ash (dross)	Seed	Zn	Zn
	HIS	No solids	Zn, Cl & F
	BH & BA Slurry	Zn, Cl & F	None (water)
	Iron Residue	Zn, Cl & F	Zn, Cl & F

Besides the zinc recovery achievable, other criteria were also used in the evaluation of the alternative neutralising agents. They included:

- ***COST:*** The cost incurred to source those neutralising agents that were purchased from an external supplier, transport costs and the loss of income in the case of using a neutralising agent that was usually sold for profit.
- ***REQUIREMENT VERSUS AVAILABILITY:*** The work would indicate the amount of neutralising agent required for the replacement of calcine. However, the availability was at times limited by plant capacity or the fact that these reagents were also in use elsewhere in the operation. In scenarios where requirement exceeded availability, only partial replacement of calcine would be possible.
- ***VOLUME OF RESIDUE GENERATED:*** A significant increase in the volume of residue would add to the disposal and rehabilitation costs.
- ***THE PRESENCE OF DETRIMENTAL IMPURITIES:*** Some of the alternative neutralising agents contained a number of impurities including halides, manganese and magnesium. Any impurities

that were not volatised in the roasters or rejected through the residues could be detrimental to the operation or place an unnecessary burden on the circuit in terms of recirculating loads.

3.1.8. FINAL LABORATORY WORK:

This portion of the work evaluated the alternative neutralising agents identified in the Preliminary Laboratory work (refer to *Section 3.1.7)*, with or without a seed recycle. *Table 5* summarises the different scenarios and their parameters.

TABLE 5: SUMMARY OF SCENARIOS AND EXPERIMENTAL PARAMETERS

Neutralising Agent	Temp (^{o}C)	pH	Residence time per reactor (min)	Seeding
Limestone	65	3.2 & 3	54	No
DRC Oxide	65	3.2 & 3	64	No
DRC Oxide	65	3.2 & 3	44	Yes, 50% recycle
Limestone & DRC Oxide	65	3.2 & 3	57	No
Limestone & DRC Oxide	65	3.2 & 3	40	Yes, 50% recycle

The experimental set-up is shown in *Figure 11* and is the same set-up as that used in the preliminary laboratory work. However, this work included a seed recycle and an acid wash. The acid wash step was performed by adding a small amount of HIS into the second reactor to reduce the pH from 3.2 to 3.0. The seed recycle was achieved by recycling 50 % (approximately 25 ml/min) of the slurry volume from the final reactor back into the first reactor with a Watson Marlow pump. The impact of a 50 % recycle was a 33.33 % decrease in the overall residence time.

'Seed' was prepared for each experiment beforehand, so that experiments were not started with empty reactors. 'Seed' generated with limestone was used for the limestone scenarios and 'seed' generated with DRC oxide was used for the DRC oxide scenarios.

500 ml slurry samples were taken from the final reactor at the end of each experiment. Settling tests were carried out on these samples under the guidance of Alister MacDonald from Mac One Agencies.

PROCEDURE FOR SETTLING TESTS:

The settling tests were performed in plexiglass cylinders with a height of 400 mm, an internal diameter of 54 mm and square flanges on both ends. The top flange had a hole of 30 mm diameter to accommodate a rubber stopper and two taper-lock syringes. The internal volume was equivalent to

2.29 ml per mm height. The cylinder had markings at 10 ml intervals. Before work commenced, masking tape was applied vertically to the cylinder in order to mark the mud-line progress during sedimentation. The tapes were removed after each test, so that the settling rate could be determined. The set-up is shown in *Figure 16*.

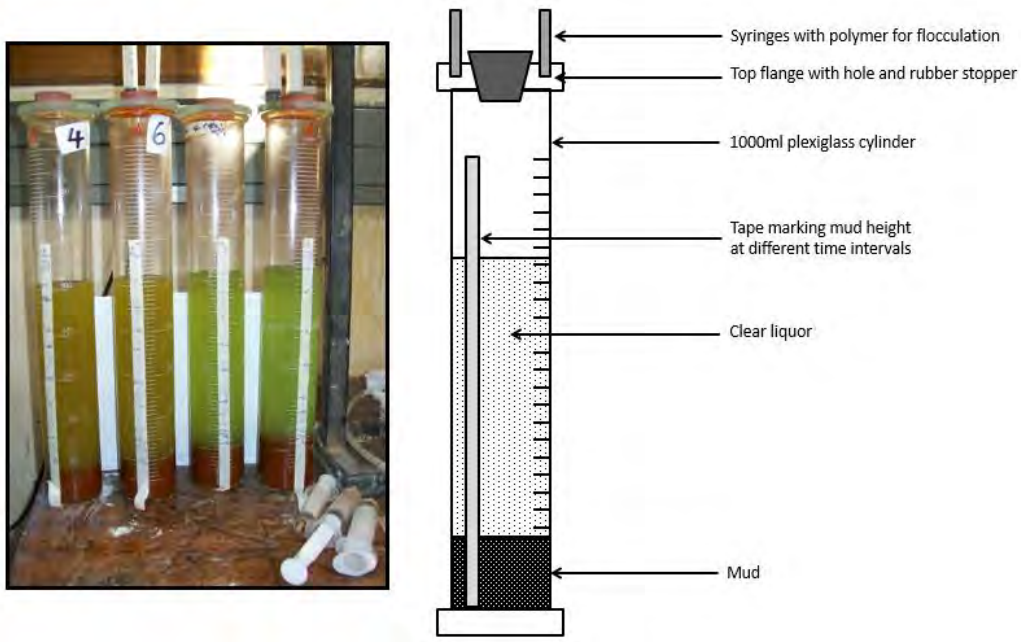


FIGURE 16: LABORATORY SET-UP FOR SETTLING TESTS PERFORMED ON SLURRY SAMPLES FROM THE FINAL REACTOR

The polymer, 920VHM, was used for flocculation. Mac One Agencies had previously evaluated a number of different polymers and had identified the one in use at Zincor as the most suitable for the application. It was not the purpose of this study to evaluate alternative polymers.

The polymer was made up to a concentration of 0.1 g/l and the required dosage was measured into the syringe. The syringe was fitted into the top flange of the cylinder by insertion of their taper-lock nozzles into the injection orifices.

Once the slurry sample had been poured into the plexiglass cylinder and the rubber stopper had been inserted, the first syringe was compressed to release the first dose of polymer. The cylinder was immediately inverted three times over and back. The first inversion had to immediately follow the polymer addition and be sufficiently vigorous for the instant dispersion of the flocculant. A second dose of polymer was added and the cylinder was again inverted three times over and back to allow for dispersion of the flocculant.

The timer was started as soon as the cylinder was placed in a vertical position after the second polymer addition. The mud-line descent was marked on the tape at regular time intervals. At the end of the experiments the cylinders were left to stand overnight to determine the final mud height. The liquor, slurry and solids SG's were also measured and recorded. The solids density was determined by using a hydrometer, while the slurry and liquor densities were determined by weighing a specific volume and dividing the mass by the volume to give units of g/cm^3. The raw data was used to determine the settling rates for the specific experimental parameters.

The settling rates were given in m/hr units. This number was determined from the difference between the start height of the slurry in the plexiglass cylinder and the mud height once the solids had settled, over the amount of time it took for the mud to reach that height.

Once the settling tests were completed the clear liquor was decanted and the mud was filtered and washed. The wet cake thickness and mass was recorded. Cakes were dried at 120 ^oC for an hour and split for various analyses. *Table 6* gives a summary of the samples taken and analyses performed.

TABLE 6: SUMMARY OF ANALYSES PERFORMED ON SAMPLES

SAMPLES:	SOLIDS ANALYSES (%):	SOLUTION ANALYSES (g/l):
Seed	Zn & Fe	Zn, Fe (II), Fe (III), H_2SO_4 & % solids
HIS	No solids	Zn, Fe (II), Fe (III) & H_2SO_4
Limestone slurry	Zn, Ca & SiO_2	% solids
DRC Oxide slurry	Zn, Ca & SiO_2	% solids
Iron Residue	Zn, Fe, Ca & SiO_2, XRD, SEM & PSD	Zn, Fe (II), Fe (III), Ca, SiO_2 & % solids

The samples for ICP and XRD (X-ray Diffraction) analyses were milled, while the samples for SEM and PSD analyses were not. The PSD analyses were carried out on dry solids, since there was no immediate on-line analysis available. The solids were slurried in an alcohol solution.

3.2. RESULTS & DISCUSSION:

3.2.1. PRELIMINARY LABORATORY WORK:

3.2.1.1. DETERMINING EXPERIMENTAL PROCEDURE & EVALUATION OF SEEDING:

The experimental set-up is shown in *Figure 11* and the experimental parameters are summarised in *Table 2*. The incoming streams were sampled prior to commencement of the experiment, with the exit stream being sampled at the end. A mass balance was performed across the circuit. The summarised results are shown in *Table 7* and the detailed mass balance can be found in *Appendix 1*.

TABLE 7: SUMMARY OF MASS BALANCE RESULTS

EXPERIMENT	Residence time (min)	'SEED'	Unaccounted (%)	Recovery (%)	Sol losses (%)	Insol losses (%)
1	69	No	16.38	90.12	0.49	9.39
2	68	Yes	19.46	92.91	0.09	7.00
3	68	Yes	11.62	92.33	0.27	7.40
4	51	Yes	11.41	93.77	0.08	6.14
5	52	Yes	7.29	94.25	0.22	5.53

The first experiment was started with empty reactors so that there was no 'seed' present in the reactors initially. Once the experiment was terminated the equipment was switched off and left overnight, only to start up again the following morning. The second experiment was run with the slurry, or 'seed', from the previous day (this procedure was repeated for experiments 3 to 5).

The pH and temperature profile remained constant for all of the scenarios, but there was a change in the residence time and the presence of 'seed'. This meant that there were three sets of experimental parameters that could be compared to one another. Experiment 1 could be compared to experiments 2 and 3 to determine the impact of 'seed'. Experiments 2 and 3 could be compared to experiments 4 and 5 to determine the impact of residence time. The comparisons were merely indicative, since the number of experiments performed were not sufficient to give conclusive results.

The unaccounted losses were high, which was an indication that steady state had not been achieved. High unaccounted losses could also be attributed to sampling inefficiencies or contamination. In addition, the high unaccounted loss in the first experiment was attributed to a lack of 'seed' at commencement of the experiment. The unaccounted loss for the second experiment remained high. It is likely that reactions continued to occur even after the first experiment was terminated, so that residual zinc was leached and accumulated in the reactors. This accumulation of zinc was not

accounted for in the mass balance, since samples were not taken again the next morning before the next experiment started. There was a decrease in the unaccounted losses for experiments 3 to 5, possibly because most of the residual zinc in the 'seed' (the slurry from the previous batch) had been leached out by this time and little accumulation occurred.

At 0.49 % the soluble loss for the first experiment was high. This was attributed to the lack of seed and the formation of a very fine precipitate with poor settling and filtration characteristics. The high insoluble loss of 9.39 % was also attributed to a lack of seed at the commencement of the experiment. In the absence of seed precipitation occurs onto the neutralising agent, resulting in coating [Claassen *et al.*, 2003].

The second experiment showed a significant decrease in the soluble loss from 0.49 to 0.09 %. The improvement was attributed to the presence of seed, which promotes agglomeration growth and the formation of coarser particles with improved dewatering characteristics [Söhnel and Garside, 1993; Claassen, 2005; Hove, 2008]. There was also a decrease in the insoluble zinc loss to 7.00 %. This could be credited to the ongoing leaching that occurred after the termination of the first experiment as well as the presence of seed. Seed provides additional surface area for precipitation so that there is less coating of unleached neutralising agent [Claassen, 2005].

Between experiments 3 to 5 there appeared to be a general increase in the zinc recovery. The improvement was attributed to the steady decrease in the insoluble zinc loss from 7.40 % in experiment 3 to 5.53 % in the final experiment. While the reason for this trend was unclear, it was possible that the 'seed' was maturing (growing in population number and size) as the days progressed.

The decrease in residence time in the last two experiments did not to appear to be significant enough to be detrimental to the zinc losses.

A Malvern Particle Size Analyser was used to determine the particle size distribution (PSD) of slurry samples from each reactor for the first two experiments (refer to *Figure 17* and *Figure 18*).

In both the 'no seed' and 'seed' scenarios in *Figure 17*, the particles increased in size up to the fourth reactor, after which they decreased slightly. This trend may be due to attrition.

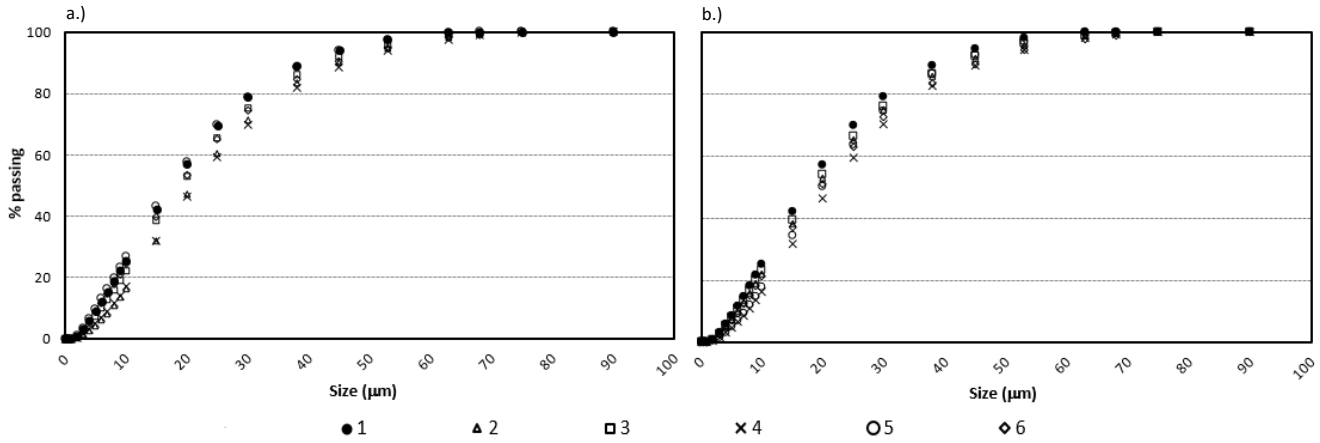


FIGURE 17: PSD RESULTS FOR THE a.) 'NO SEED' AND b.) 'SEED' SCENARIOS FOR SAMPLES FROM EACH REACTOR

A comparison of the PSD results from both the 'no seed' and 'seed' scenarios showed that there was no significant difference in particle size between the samples from reactors 1 to 4, but a small increase was observed for particles in the presence of seed from reactors 5 and 6 (refer to *Figure 18*). The graphs show that there was an increase in particle size in the larger size fractions (between 10 and 20 µm). This supports the results from the mass balance (refer to *Table 7*) that showed a lower soluble zinc loss in the presence of seed. The fact that the size increase was only noticeable in the last two reactors hints at the significance of residence time in particle growth and agglomeration [Söhnel and Garside, 1993; Lewis, 2009 and Claassen, 2005].

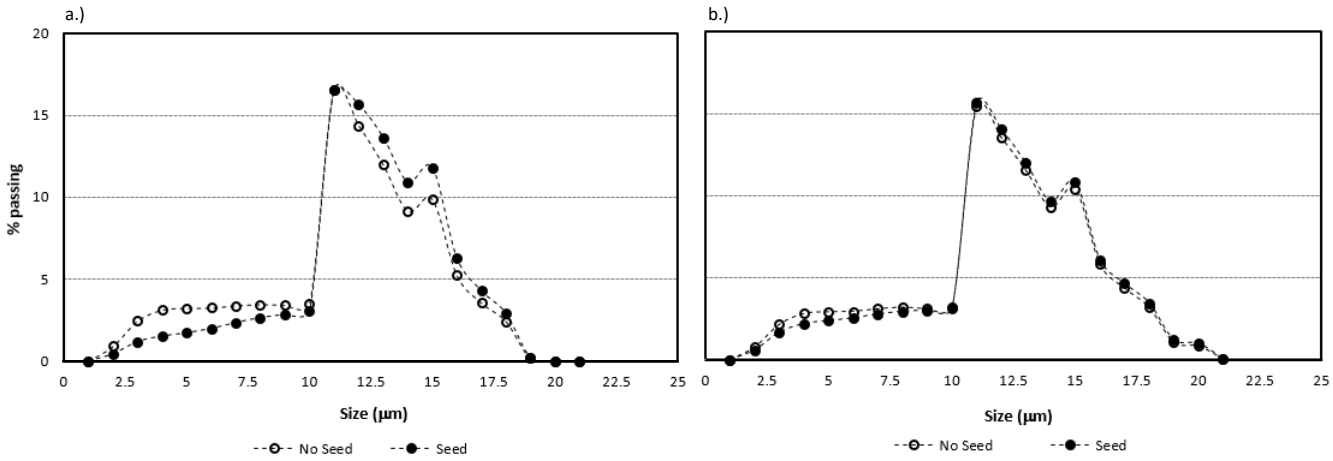


FIGURE 18: FREQUENCY DISTRIBUTION CURVES COMPARING THE PSD RESULTS FOR THE 'NO SEED' AND 'SEED' SCENARIOS FOR SAMPLES FROM A.) THE FIFTH AND B.) THE SIXTH REACTORS

Despite the limitations of the experimental work, the tentative results appeared to demonstrate that the presence of seed reduced both the soluble and insoluble zinc losses by supporting particle growth and reducing coating of zinc-rich neutralising agent.

3.2.1.2. IDENTIFYING ALTERNATIVE NEUTRALISING AGENTS:

Refer to *Figure 15* for the experimental set-up. Besides zinc recovery, the neutralising agents were also evaluated according to the following criteria:

- ***THE COST:*** DRC oxide, slaked lime and limestone were sourced externally. DRC oxide was the most costly reagent, due to the high zinc content and high transportation costs. Slaked lime came at a much higher cost than limestone. No cost was incurred to source Basic Zinc Sulphate (BZS), Effluent Treatment Plant (ETP) Thickener U/F, Baghouse Dust and Brown Ash, since they were either 'waste' products or by-products of the Zincor operation. However, an operational cost would be incurred. In the case of the bag house dust and brown ash, the 'cost' would be the loss of income from not selling the product for the zinc content.
- ***REQUIREMENT VERSUS AVAILABILITY:*** The volume of BZS available from the bleed plant was at most 5 m^3/hr, since half of it was already in use as a filter aid on the Pb/Ag belt. The Oxide Washing Plant could supply at most 6 m^3/hr of oxide slurry consistently. Both lime and limestone were used for neutralisation in other areas of the plant, so that there would be a limitation on the supply at times. In scenarios where the requirement for neutralisation exceeded the volume of neutralising agent available, only partial replacement of calcine would be possible.
- ***VOLUME OF RESIDUE GENERATED:*** The use of calcium-based neutralising agents typically generate a large volume of residue, adding to the disposal and rehabilitation costs. Lime, limestone, BZS and ETP Thickener U/F all contained a large amount of gypsum.
- ***THE PRESENCE OF DETRIMENTAL IMPURITIES:*** The ETP Thickener U/F and BZS contained a number of impurities, which would likely leach at the typical operating conditions maintained in the Iron Removal Stage. The chloride contained in the brown ash and bag house dust originated from the use of ammonium chloride in the Zincor furnaces. High levels of chloride in solution could accelerate the corrosion of plant equipment. DRC oxide contained fluoride. High levels of fluoride in the purified solution could cause sticky deposits, making the cathodes very difficult to strip. While the majority of fluoride present in the DRC oxide was volatilised in the roasters or rejected through the iron residue, there was a concern that an increase in DRC addition could result in elevated fluoride levels in the purified solution.

Each potential neutralising agent was evaluated according to the above criteria on the basis of treating 1 m^3 of HIS. The results from the comparison, together with the results from the mass balance, are summarised in *Table 8* and apply to the discussion that follows. The detailed mass balance can be found in *Appendix 1.*

TABLE 8: OUTCOME OF MASS BALANCE & COMPARISON OF NEUTRALISING AGENTS ACCORDING TO SELECTED CRITERIA

	DRC Oxide	ETP U/F	Basic Zinc Sulphate	Lime	Limestone	Baghouse & Brown Ash
OUTCOME OF MASS BALANCE: ZINC RECOVERY AND LOSSES						
Unaccounted (%)	-7.91	-6.96	-3.11	-10.04	-6.35	-3.63
Zn recovery (%)	96.84	95.64	98.24	96.22	98.08	94.29
Soluble Zn losses (%)	0.38	0.43	0.52	0.40	0.55	0.16
Insololuble Zn losses (%)	2.78	3.93	1.23	3.38	1.37	5.54
COMPARISON OF NEUTRALISING AGENTS ACCORDING TO SELECTED CRITERIA						
Cost to neutralise 1m^3 HIS (R)	322.78	N/A	N/A	35.42	7.67	49.14
Requirement of neutralising agent (m^3/1m^3 of HIS)	0.12	2.61	0.57	0.11	0.29	0.05
Availability of neutralising agent (m^3/1m^3 of HIS)	0.10	1.00	0.06	0.05	0.07	0.20
Residue generated to neutralise 1 m^3 of HIS (m^3)	0.14	0.75	0.29	0.28	0.21	0.18
Rejection of impurities to residue (%)	F 99.99	Mn 13.20 Mg 0.79	Mn 2.70 Mg 0.82	N/A	N/A	F 99.17 Cl 1.29

The unaccounted losses for all the experiments were negative, which indicated that the zinc in the input stream exceeded the zinc in the exit stream. This was probably as a result of the experimental procedure that was followed. Each experiment was started with some seed in the first reactor. While the seed was sampled and considered during the mass balance, the results indicate that not all of the contained zinc was accounted for.

DRC OXIDES:

This scenario ranks somewhere in the middle in terms of zinc recovery, soluble and insoluble zinc losses. It generated the lowest volume of residue. Since the same volume of wash water was used throughout, a low residue volume gave a high wash ratio. The relatively low soluble zinc loss could likely be attributed to the high wash ratio. The insoluble loss was likely due to coating of the zinc-rich neutralising agent by iron precipitate.

DRC oxide was by far the most costly reagent. The supply was limited by the plant capacity of the Oxide Washing Plant and was slightly less than the requirement for complete replacement of calcine. Practically all of the fluoride was rejected via the iron residue at the experimental conditions.

Since the DRC oxide had been used for neutralisation in the Iron Removal Stage for a number of years, it had been proven as a suitable replacement or supplement for calcine.

EFFLUENT TREATMENT PLANT (ETP) THICKENER UNDERFLOW:

The use of ETP thickener underflow for neutralisation performed poorly with regards to zinc recovery and zinc losses. With a high calcium content it was not surprising that this scenario generated by far the highest volume of residue. Calcium-based neutralising agents also typically generate a very fine precipitate. The high volume of residue with the corresponding low wash ratio, together with the potentially fine nature of the precipitate, supported the high soluble zinc loss determined in the mass balance. ETP thickener underflow contained approximately 12 % zinc, so that the insoluble zinc loss was likely due to coating of the unleached neutralising agent with iron precipitate. The requirement for neutralisation was much higher than for all the other scenarios.

Since ETP thickener underflow was a waste product there was no cost to source it. There would be a small operating cost associated with its use, but this would be minimal compared to some of the other potential neutralising agents.

Iron, manganese, magnesium, copper, cobalt and cadmium were the main impurities present in ETP thickener underflow. Almost all of these impurities were leached under the experimental conditions. Even though the impurities would probably be removed again in the Iron Removal Stage, the Purification and Effluent Treatment plants, the recycling load would place an unnecessary burden on the circuit.

This neutralising agent was not considered a suitable supplement or replacement for calcine, due to the mediocre performance in terms of zinc recovery and the presence of impurities.

BASIC ZINC SULPHATE:

This scenario had the best zinc recovery. The relatively high soluble zinc loss may be attributed to the high solids loading and corresponding low wash ratio. Claassen (2002) found that the gypsum contained in the BZS acted as a filter aid. With good filtration, an increase in the wash ratio would almost certainly reduce the soluble zinc loss. BZS contained approximately 12 % zinc, resulting in some zinc loss through coating with iron precipitate. The high reactivity of this reagent may have contributed to the good performance in terms of insoluble zinc loss (Claassen, 2002).

Since BZS was a ‘waste’ product from the bleed plant, no cost was incurred to source it. Any operating cost allocated to its use as a neutralising agent would be very small compared to the cost of some of the other alternative neutralising agents. The availability was far below the requirement, due to the

limitations of the Magnesium Bleed Plant and the fact that this cake was already in use as a filter aid on the Pb/Ag belt. Very little of the manganese and magnesium present in the BZS cake was rejected via the residue, which would cause a circulating load and place an unnecessary burden on the overall operation.

Despite the excellent recovery achievable, very little of the BZS cake was available for neutralisation in the Iron Removal Stage, so that it would not be evaluated further.

SLAKED LIME:

The use of slaked lime for neutralisation lead to a mediocre performance in terms of zinc recovery. The volume of residue generated was relatively high, resulting in a low wash ratio. Claassen (2002) attributed the high soluble zinc loss to the entrainment of zinc-rich solution in the precipitate. Claassen credited the high insoluble zinc loss to the difficulty in controlling the HIS supersaturation levels when using lime for neutralisation.

Lime was a costly reagent compared to limestone. Its availability as a neutralising agent was limited by the slaking capacity of the plant and its use in the Magnesium Bleed operation and the Effluent Treatment Plant. It contained no detrimental impurities.

Lime was not considered a suitable replacement for calcine since it had a mediocre performance in terms of zinc recovery, was very costly and had limited availability.

CHEMICALLY PRECIPITATED $CaCO_3$ (LIMESTONE):

The use of limestone as a neutralising agent achieved an excellent zinc recovery. The soluble loss was relatively high. As with all the other calcium-based neutralising agents, the reason was attributed to the high volume of residue generated and the impact that this had on the wash ratio. Claassen (2002) attributed the low insoluble zinc loss to good reactivity and improved control of HIS supersaturation levels when using limestone.

Besides ETP thickener underflow and BZS (which were both waste products), limestone was the cheapest reagent. Its availability was limited by the capacity of the slurrying plant and its use for neutralisation in the Effluent Treatment Plant. This reagent contained a small amount of sodium, but no other detrimental impurities.

Limestone was considered a suitable replacement for calcine due to an excellent zinc recovery, low cost and lack of detrimental impurities.

BAGHOUSE DUST AND BROWN ASH:

This scenario used a combination of baghouse dust and brown ash (or furnace dross) as a neutralising agent. It had the poorest zinc recovery. The volume of the residue generated was relatively low, so that little wash water was needed for efficient washing. This neutralising agent had a zinc content of approximately 83 %, some of which was present as metallic zinc, so that coating by iron precipitate resulted in a very high insoluble zinc loss.

This reagent was typically sold for the zinc content, so that the 'cost' incurred was equivalent to the loss of income. The high zinc content made it an expensive neutralising agent. This was the only scenario where availability of the neutralising agent was not limited and complete replacement of calcine would be possible. These materials contained halides in the form of fluoride and chloride. The bulk of the fluoride was rejected via the iron residue, but almost all of the chloride was dissolved under these experimental conditions. Chloride in solution could lead to the corrosion of process equipment.

Taking into account the dismal recovery achieved, the high cost and the presence of potentially detrimental impurities, this neutralising agent was not considered a suitable replacement or supplement for calcine.

SUMMARY:

The initial laboratory trials identified DRC oxide and chemically precipitated $CaCO_3$ as the most suitable supplements and/or replacements for calcine. These reagents would be further evaluated, together with a seed recycle, in the next portion of the experimental work.

3.2.2. FINAL LABORATORY WORK:

3.2.2.1. OUTCOME OF MASS BALANCE:

This portion of the laboratory work evaluated DRC oxide and limestone as replacements for calcine, together with a seed recycle. Refer to *Figure 11* for the experimental set-up. The summarised results from the mass balance are shown in *Table **9***. The complete mass balance is available in *Appendix 2.*

TABLE 9: MASS BALANCE RESULTS FOR THE EVALUATION OF ALTERNATIVE NEUTRALISING AGENTS AND A SEED RECYCLE

EXPERIMENT:	Unaccounted (%)	Zn recovery (%)	Sol Zn losses (%)	Insol Zn losses (%)	Residue Volume (cm^3)
Limestone	5.23	95.10	3.66	1.24	364
DRC Oxide	1.55	95.96	1.12	2.91	165
DRC Oxide (with seed recycle)	10.03	94.05	2.27	3.68	236
Limestone & DRC Oxide	9.69	96.20	3.39	0.42	250
Limestone & DRC Oxide (with seed recycle)	9.26	97.02	2.46	0.52	330

GENERAL:

The unaccounted losses were high and positive, which indicated that steady state had not been reached and that the amount of zinc in the exit streams exceeded the amount of zinc in the input streams. This could be attributed to the experimental procedure followed and inaccuracies in sampling and analyses. As in the preliminary experimental work, the equipment was simply switched off at the end of the experiment and started up again the next morning. It was likely that leaching continued even after the experiment was terminated, so that there was some accumulation of zinc. Since exit samples were taken immediately after an experiment, they did not account for this accumulation.

There was an initial increase in the precipitate volume with the implementation of a seed recycle. The precipitate volume should reach steady state over time, but the laboratory work was terminated before this was achieved. Since the same amount of wash water was used throughout, an increase in the iron residue related to a decrease in the wash ratio and an increase in the soluble zinc loss. Even though the presence of seed is known to improve the dewatering characteristics of the precipitate [Claassen, 2005; Hove, 2008], an equivalent increase in wash water addition would be required to accommodate for an increase in precipitate volume as a result of a seed recycle. The residue volume also had an environmental impact, since a large volume of residue increased the disposal and rehabilitation costs.

LIMESTONE:

Quite a bit of 'frothing' occurred with the use of limestone as a result of CO_2 emissions from the neutralisation reaction (see *Reaction 12*). This would need to be considered if limestone addition is ever implemented on a plant scale.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \qquad (12)$$

This scenario had the second lowest recovery. The poor performance in recovery was largely attributed to the high soluble zinc loss. The use of limestone for neutralisation generated a large volume of gypsum, which contributed to this residue being the most voluminous of all. The corresponding low wash ratio was likely the cause of the high soluble zinc loss.

DRC OXIDE:

In the experiments utilising DRC oxide for neutralisation, the scenario with a seed recycle had a poorer zinc recovery than that without. Both the soluble and insoluble zinc losses were higher. The higher soluble loss was as a result of an increase in the residue volume and the corresponding low wash ratio.

The presence of seed typically reduces the insoluble zinc loss. However, in this case the insoluble zinc loss increased with the addition of a seed recycle. While the reason was not clear, it may be related to residence time. The seed addition was achieved via a 50 % volume recycle from the final reactor back into the first reactor, decreasing the residence time by 33.33 %. Haegele *et al*. (1992) found that an increase in residence time improves the quality of the precipitate. It appears that residence time is a key parameter that needs to be considered. Alternatively, the pH in the second reactor may have drifted. The Zincor process was highly sensitive to pH (refer to *Figure 6*) so that even a very small change in the pH profile could result in a complete change in the precipitate composition and morphology.

DRC OXIDE AND LIMESTONE COMBINATION:

Both scenarios (with and without a seed recycle) gave excellent zinc recoveries. The improvement in recovery was attributed to the significant decrease in the insoluble portion of the zinc loss.

The soluble zinc loss was relatively high for both scenarios (with and without a seed recycle), which was due to the high residue volumes and the associated low wash ratios. The use of limestone for neutralisation generated gypsum, which is voluminous. The addition of a seed recycle increased the residue volume even further.

The combination of limestone and DRC oxide for neutralisation resulted in very low insoluble zinc losses, even lower than that achieved when using only limestone for neutralisation. Claassen (2002) had combined Basic Zinc Sulphate with DRC oxide for neutralisation and also achieved significantly lower insoluble zinc losses. He had attributed the improvement to the higher reactivity of the combination of these neutralising agents compared to calcine. Since limestone is also a calcium-based

neutralising agent (like Basic Zinc Sulphate), the reason for the good performance in this experimental work may be similar.

There was an increase in the insoluble zinc loss with the addition of the seed recycle. This was possibly related to the decrease in residence time as a result of the seed recycle.

3.2.2.2. OUTCOME OF PSD ANALYSES:

The particle size distribution was determined for the limestone and DRC oxide neutralising agents, as well as the precipitate from the limestone-only and oxide-only runs, using a Malvern Particle Size Analyser. The results are presented in *Figure 19*.

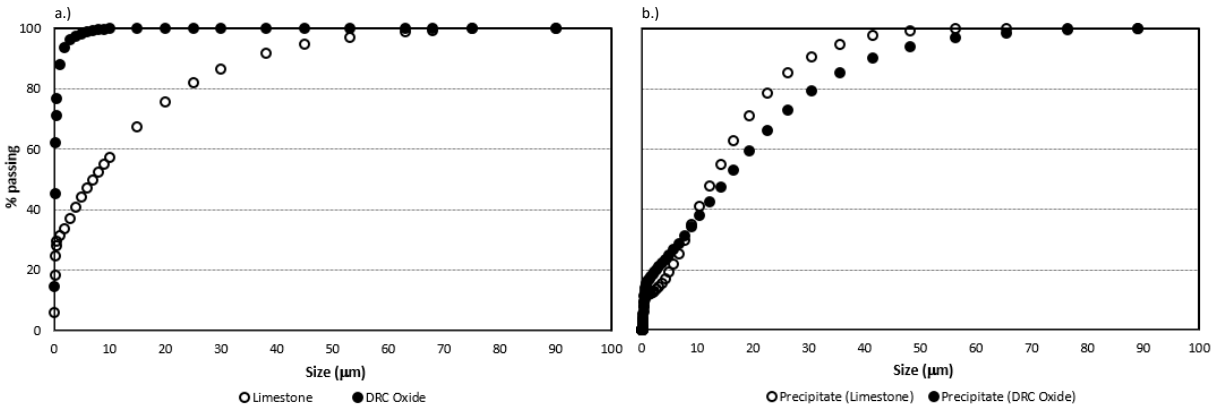


FIGURE 19: COMPARISON OF PSD FOR a.) LIMESTONE AND DRC OXIDE NEUTRALISING AGENTS AND b.) PRECIPITATE FROM LIMESTONE-ONLY AND DRC OXIDE-ONLY RUNS

Figure 19 (a) shows that the limestone was considerably coarser than the DRC oxide. In fact, the D_{50} for the limestone was 6.8 μm compared to only 0.23 μm for the DRC oxide.

From *Figure 19 (b)* it appeared that the precipitate generated from neutralisation with limestone was coarser below approximately 10 μm. However, above 10 μm the precipitate generated from neutralisation with DRC oxide was coarser. The D_{50} for the limestone scenario was 13 μm and the D_{90} was 30 μm, while the D_{50} for the DRC oxide scenario was 16 μm with a D_{90} of 41 μm.

Although the DRC oxide as a neutralising agent was much finer than the limestone, its use appeared to result in the formation of a coarser precipitate. While the reason for this phenomenon was not clear it may have had something to do with the fact that a fine neutralising agent has a higher

utilisation efficiency or reactivity (refer to *Section 2.3.4*). A coarser precipitate is known to have better dewatering characteristics, giving lower soluble zinc losses [Claassen, 2005]. These results support the finding from the mass balance in *Section 3.2.2.1,* where experiments utilising DRC oxide as a neutralising agent had lower soluble losses than those utilising limestone. While the high soluble losses were attributed mostly to the low wash ratio, one cannot ignore the effect of particle size.

3.2.2.3. OUTCOME OF SETTLING TESTS:

The experimental procedure for settling tests is outlined in *Section 3.1.8*. A settling test was performed on the precipitate from each of the scenarios and the results are summarised in *Table 10*.

TABLE 10: SETTLING RATE FOR EACH OF THE SCENARIOS USING DRC OXIDE, LIMESTONE AND A SEED RECYCLE

EXPERIMENT:	FLOC DOSAGE (ppm)	LIQUOR SG	SETTLING RATE (m/hr)
$CaCO_3$	2	1.22	0.76
	4		1.06
DRC OXIDE	2	1.27	2.73
	4		3.88
DRC OXIDE (SEED)	2	1.24	2.94
	4		4.92
DRC OXIDES & $CaCO_3$	2	1.23	3.27
	4		5.04
DRC OXIDE & $CaCO_3$ (SEED)	TOO SLOW, ABORT TEST		

The use of limestone for neutralisation generated a large volume of fine precipitate (refer back to *Table **9*** and *Figure 19 (b)*). The poor settling rate was, therefore, attributed to the fineness of the particles and possibly particle crowding [Claassen and Sandenbergh, 2006].

The precipitate generated using DRC oxide for neutralisation had a relatively good settling rate. The settling rate improved in the presence of seed.

The scenarios using a combination of DRC oxide and limestone gave an excellent zinc recovery (refer back to *Table **9***). However, the soluble zinc loss was very high. Since the settling rate for this scenario was very good, the reason for the high soluble loss was probably related to the high residue volume and corresponding low wash ratio. An increase in the wash water addition (to accommodate for the high residue volume) would probably reduce the soluble zinc loss.

The precipitate resulting from neutralisation with a combination of DRC oxide and limestone had a relatively good settling rate. The addition of a seed recycle resulted in very poor settling, possibly due to particle crowding. *Table **9*** shows that this scenario generated a large volume of residue.

In each of the settling tests an increase in flocculant dosage improved the settling rate. The liquor density also impacted on the settling rate, with a high liquor density hindering settling. It is for this reason that dilution of the thickener feed was often recommended to improve settling. However, water addition was often restricted by the plant solution inventory.

3.2.2.4. OUTCOME OF XRD ANALYSES:

A precipitate sample from each of the scenarios was submitted for XRD analyses. The results are summarised in *Table 11*.

TABLE 11: XRD RESULTS FOR THE EVALUATION OF ALTERNATIVE NEUTRALISING AGENTS AND A SEED RECYCLE

COMPOUND:	LIMESTONE:	DRC OXIDE:	DRC OXIDE (SEED):	DRC OXIDE & LIMESTONE:	DRC OXIDE & LIMESTONE (SEED):
Anglesite - $PbSO_4$ (%)		29.24	17.11	5.67	4.19
Bassanite - $CaSO_4 0.5H_2O$ (%)	100			77.55	79.22
Gunningite - $ZnSO_4H_2O$ (%)		28.99	15.76		
Plumbo-jarosite - $PbFe_6(SO_4)_4(OH)_{12}$ (%)		32.12	51.99	10.38	16.59
Magnetite - Fe_3O_4 (%)		9.66	15.14	6.41	

Bassanite was present in the residue samples where limestone was used for neutralisation. It has been suggested that the formation of gypsum starts with the formation of tiny crystals of Bassanite. This compound is extremely fine and is likely to have very poor settling characteristics. The presence of Bassanite probably contributed to the poor settling experienced in some of the experiments utilising limestone for neutralisation. Additional residence time to allow for particle growth could potentially result in the formation of a coarser precipitate with improved settling characteristics [Söhnel and Garside, 1993; Lewis, 2009; Claassen, 2005].

Two iron complexes, namely Magnetite and Plumbo-Jarosite, were identified in the residue of the scenarios utilising DRC oxide for neutralisation. However, the formation of Magnetite was not thermodynamically possible at these experimental conditions (refer back to *Figure 6*). Magnetite is typically formed from ferrous at a pH of 9 or more, so that this complex was probably Ferrihydrite. Jarosite is formed during the oxidation of iron sulphides and is a common waste product from the

purification and refining of zinc. Plumbo-Jarosite is a variety of Jarosite where the potassium is replaced with lead. The formation of Plumbo-Jarosite was not surprising, since the DRC oxide contained an average of approximately 9 % Pb.

In addition to the iron complexes, these samples also contained Gunningite and Anglesite. Gunningite is a mineral in the Kieserite group and Anglesite is a poorly soluble lead sulphate mineral. Lead typically forms soluble complexes with carbonate, which is why Anglesite was not present in the sample where only limestone was utilised for neutralisation.

3.2.2.5. OUTCOME OF SEM ANALYSES:

SEM (Scanning Electron Microscopy) images of selected precipitate samples from the final laboratory work are shown in *Figure 20*, *Figure 21*, *Figure 22* and *Figure 23*. The precipitate resulting from neutralisation with limestone appeared to be amorphous in nature (refer to *Figure 20* and *Figure 23*). Amorphous particles do not settle well and typically retain zinc–rich solution. The images also showed the presence of fine particles, which do not have good settling characteristics. The amorphous nature and fineness of the precipitate would contribute to high soluble zinc losses and poor settling, supporting the results summarised in *Table **9*** and *Table 10*. While the high soluble zinc loss of the scenarios utilising limestone for neutralisation was initially attributed mostly to the low wash ratio, the effect of particle size and morphology cannot be ignored.

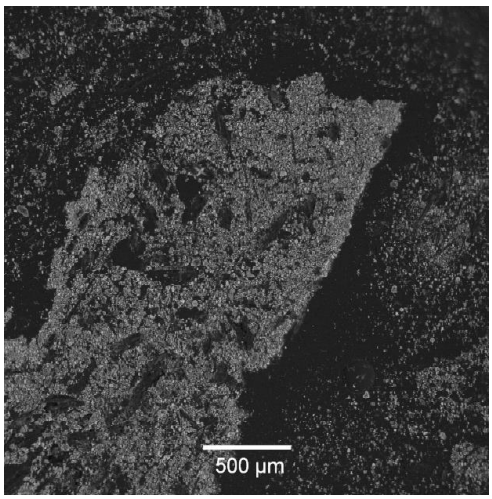


FIGURE 20: A SEM IMAGE OF PRECIPITATE FROM AN EXPERIMENT UTILISING ONLY LIMESTONE FOR NEUTRALISATION

The precipitate resulting from neutralisation with DRC oxide appeared to be more defined and denser (refer to *Figure 21* and *Figure 22*), supporting the lower soluble losses and improved settling rates of these scenarios compared to the scenarios using limestone (refer to *Table **9*** and *Table 10*).

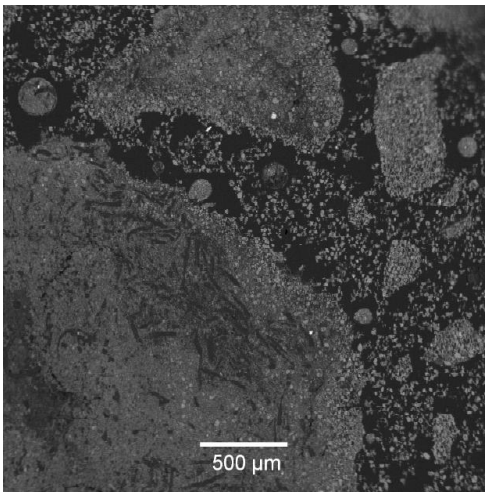


FIGURE 21: A SEM IMAGE OF PRECIPITATE FROM AN EXPERIMENT UTILISING ONLY DRC OXIDE FOR NEUTRALISATION

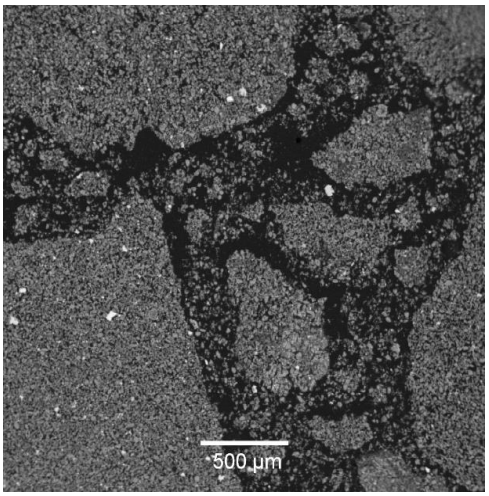


FIGURE 22: A SEM IMAGE OF PRECIPITATE FROM AN EXPERIMENT UTILISING DRC OXIDE FOR NEUTRALISATION WITH A SEED RECYCLE

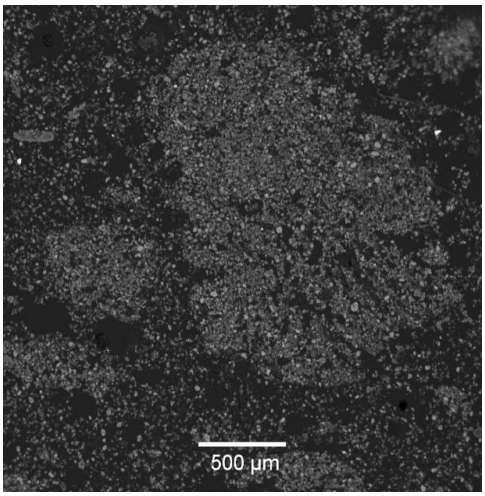


FIGURE 23: A SEM IMAGE OF PRECIPITATE FROM AN EXPERIMENT UTILISING A COMBINATION OF LIMESTONE AND DRC OXIDE FOR NEUTRALISATION WITH A SEED RECYCLE

4. PLANT TRIAL:

4.1. METHODOLOGY:

4.1.1. SCOPE OF WORK:

The plant trial evaluated the implementation of a seed recycle. The seed recycle rate was gradually increased over the 4-week period.

4.1.2. LIMITATIONS:

The plant operation was a complex and dynamic environment with multiple parameters changing constantly and simultaneously. An increase was observed in the residue volume after each increase in the seed recycle set-point. The residue volume would reach a plateau once the operation was at steady state. The fact that this hadn't occurred during the 4-week period indicated that steady state had not been achieved. For this reason the results obtained during the course of the plant trial were not considered conclusive. Instead, some observations were made and tentative conclusions drawn in order to support a further more detailed study.

4.1.3. EXPERIMENTAL SET-UP:

The plant trial was carried out in the Iron Removal Stage at Zincor. A detailed process description can be found in *Section 1.2.2* of the introductory chapter. *Figure 24* is a schematic of the Zincor Iron Removal Stage and indicates the seed recycle, as well as the sample points.

Seeding was achieved by recycling solids from the pump suction of the thickener underflow via a pipeline into the first reactor of the Iron Removal Stage. There was a screen box in the pump suction line to remove grit and prevent choking. An automatic valve was installed in this line to regulate the flowrate of the seed recycle to a desired set-point. The automatic valve was set up to flush the line hourly by fully opening the valve and increasing the flow to the maximum set-point for a minute in order to keep the line clear and prevent solids build-up. The volume of seed added while flushing was insignificant compared to the overall daily volume.

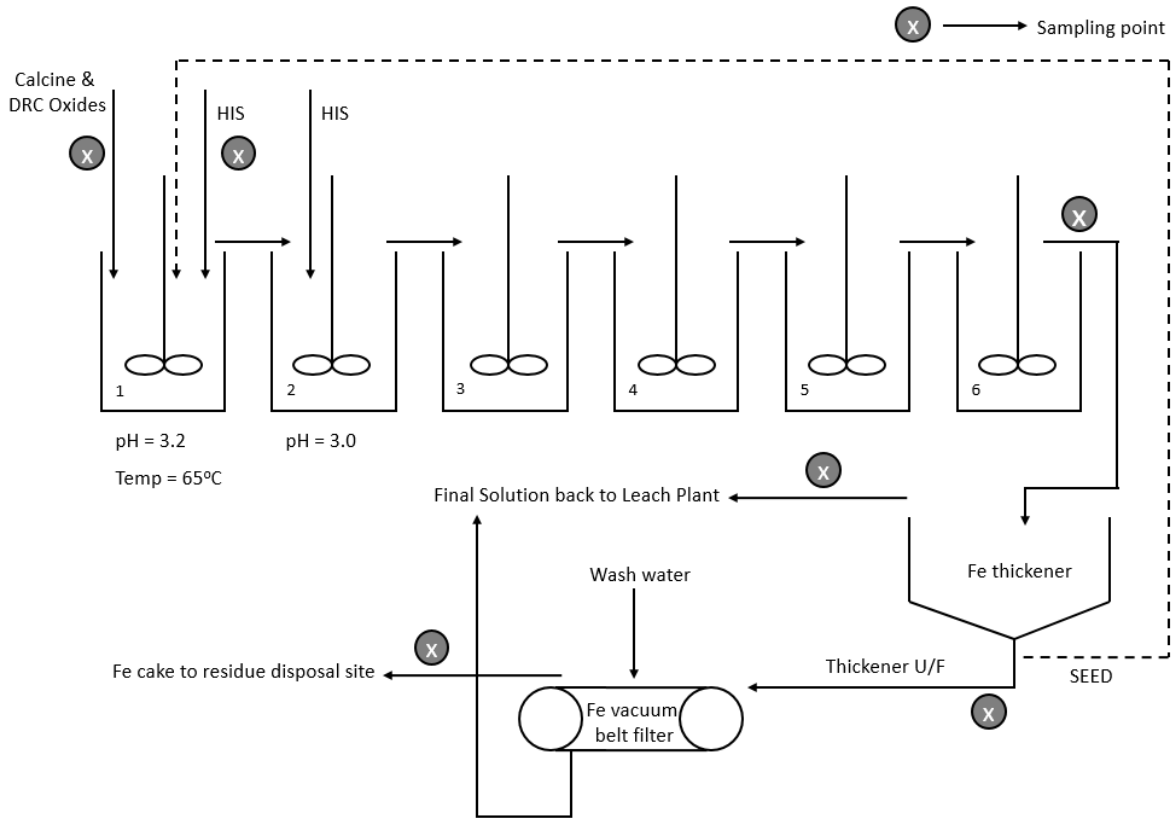


FIGURE 24: EXPERIMENTAL SET-UP FOR THE PLANT TRIAL INDICATING THE SEED RECYCLE AND SAMPLE POINTS

4.1.4. EXPERIMENTAL PROCEDURE:

The seeding program was run over a period of approximately four weeks. The purpose of the first week was to establish a base case. It was vital to operate the plant as it would under typical conditions.

Seeding was implemented at the end of the first week. 'Low', 'medium' and 'high' scenarios were set for the seed recycle, with the 'high' scenario equivalent to approximately 50 % of the flowrate from the thickener underflow. The flowrate from the thickener underflow was typically 12 m^3/hr, so that the maximum set-point for the seed recycle was set at 6 m^3/hr. The plant was run on each set-point for approximately a week. At the end of each week the seeding set-point was increased to the next level. No sampling was done for at least 24 hours after a change was made. The test programme is shown in *Table 12*.

Since seeding had never been run for an extended period before, it was uncertain what the plant limitations were and what the impact on the operation would be. Therefore, the plant conditions were monitored around the clock during this period.

TABLE 12: PARAMETERS EMPLOYED FOR THE PLANT TRIAL (SEPTEMBER TO OCTOBER 2011)

DATE:	SEED:	COMMENTS:
29-Sep-11	None	BASE CASE
30-Sep-11	None	BASE CASE
1-Oct-11	None	BASE CASE
2-Oct-11	None	BASE CASE
3-Oct-11	2 m^3/hr	No sampling
4-Oct-11	2 m^3/hr	No sampling
5-Oct-11	2 m^3/hr	LOW
6-Oct-11	2 m^3/hr	LOW
7-Oct-11	2 m^3/hr	LOW
8-Oct-11	2 m^3/hr	LOW
9-Oct-11	2 m^3/hr	LOW
10-Oct-11	4 m^3/hr	No sampling
11-Oct-11	4 m^3/hr	MEDIUM
12-Oct-11	4 m^3/hr	MEDIUM
13-Oct-11	4 m^3/hr	MEDIUM
14-Oct-11	4 m^3/hr	MEDIUM
15-Oct-11	4 m^3/hr	MEDIUM
16-Oct-11	6 m^3/hr	No sampling
17-Oct-11	6 m^3/hr	HIGH
18-Oct-11	6 m^3/hr	HIGH
19-Oct-11	6 m^3/hr	HIGH

The first two reactors in the Iron Removal Stage had double-bladed agitators, while the remaining reactors only had single bladed agitators. Seeding would temporarily result in an increased solids loading into the circuit until steady state had been reached. Due to the decrease in mixing intensity between the third and final reactors, one concern was that a build-up of solids could occur in these reactors. The same concern was valid for the Iron Thickener, which could result in the thickener rake motors tripping. To prevent this from occurring, the following parameters were closely monitored:

- The settling rate of the thickener feed was monitored by doing settling tests every two hours;
- The depth of the solids bed inside the thickener was measured every two hours;
- The torque on the thickener rakes was monitored with an instrument and displayed on the SCADA (Supervisory Control and Data Acquisition), which is a computer system used to control and monitor the process. The rakes would automatically trip out if the torque exceeded the maximum set-point. The torque was logged every two hours; and
- The belt speed and wash water addition (or wash ratio) were closely monitored and adjusted to accommodate for additional solids reporting to the belt filters. This was only done when the plant inventory allowed it.

The parameters that influenced the thickener performance were of the highest priority, since it would be the first sign that adjustments to the seed recycle were needed.

4.1.5. SAMPLING & ANALYSES:

Zincor operated a three-shift system. Samples of each feed and exit stream were taken on each shift and a composite for the 24-hour period was submitted for analyses. The sample points are indicated on the schematic in *Figure 24*. The thickener feed sample was taken in the launder after the flocculant addition point. *Table 13* summarises the samples taken and the relevant analyses performed.

Since DRC oxides contain fluoride, there was a concern that an increase in the DRC oxide addition would result in elevated fluoride levels in the circuit. For this reason the chemical analyses included fluoride. Elevated fluoride levels resulted in localised corrosion of the cathode substrate and exacerbated sticky deposits in the electrowinning circuit. Zincor did not traditionally have a problem with high halide levels in the circuit, since the majority of halides were volatised during the roasting step and the remainder were rejected through the iron residue. However, with an increase in DRC oxide addition into the Iron Removal Stage, the fluoride levels did at times increase. DRC oxides contained approximately 0.03 % fluoride, which was far higher than any of the other raw materials.

The chemical analyses, volumes and masses were used to perform a mass balance across the Iron Removal circuit. The outcome of the mass balance, together with the other results and observations, were used to draw tentative conclusions with regards to the impact of seeding on the process.

4.1.6. MASS BALANCE:

The purpose of the mass balance was to determine the zinc recovery, soluble and insoluble zinc losses, as well as the degree of fluoride rejection via the iron residue. A simplified schematic illustrating the principles followed in the mass balance is shown in *Figure 25*.

The zinc balance is carried out according to *Equation 8*.

$$Zn_{IN} = Zn_{OUT}$$

$$Zn_{Calcine} + Zn_{DRC\ oxide} + Zn_{HIS} + Zn_{seed\ recycle} = Zn_{Fe\ Slurry} + Zn_{seed\ recycle} \quad (8)$$

$$Zn_{Calcine} + Zn_{DRC\ oxide} + Zn_{HIS} = Zn_{Fe\ Slurry}$$

TABLE 13: SUMMARY OF SAMPLES TAKEN AND ANALYSES PERFORMED

SAMPLES:	SAMPLING PROCEDURE:	SAMPLING PREPARATION:	RAW DATA LOGGED:	ANALYSES:	CHEMICAL ANALYSES:	
					SOLIDS (%)	SOLUTION (ppm or g/l)
Tanks 1, 2, 4 & 6	Take slurry sample on M/S	Filter; wash & dry cake	Slurry, liquor & solids SG; wet & dry cake mass; % solids	PSD	Zn	Zn
HIS	Take a sample on each shift and composite over 24 hrs		Flowrate (No. 1 and 2 reactor)			Zn & F
CALCINE SLURRY	Take a sample on each shift and composite over 24 hrs	Filter; wash & dry cake	Slurry, liquor & solids SG; wet & dry cake mass; % solids; flow (m^3 and dmt)		Zn & F	Zn & F
OXIDE SLURRY	Take a sample on each shift and composite over 24 hrs	Filter; wash & dry cake	Slurry, liquor & solids SG; wet & dry cake mass; % solids; flow (m^3 and dmt)		Zn & F	
THICKENER FEED	Take slurry sample on M/S (in launder after floc addition point)			Settling & filtration		
THICKENER OVERFLOW (FINAL SOLUTION)	Take a sample on each shift and composite over 24 hrs		pH, temp. & solution SG			Zn & F
THICKENER UNDERFLOW (SEED)	Take a sample on each shift and composite over 24 hrs	Filter; wash & dry cake	Slurry, liquor & solids SG; wet & dry cake mass; % solids		H_2O, Zn & F	Zn & F
Fe CAKE	Take a sample on each shift and composite over 24 hrs	Dry cake	Wet and dry mass; Solids SG	XRD & SEM-EDX	H_2O, Zn & F	

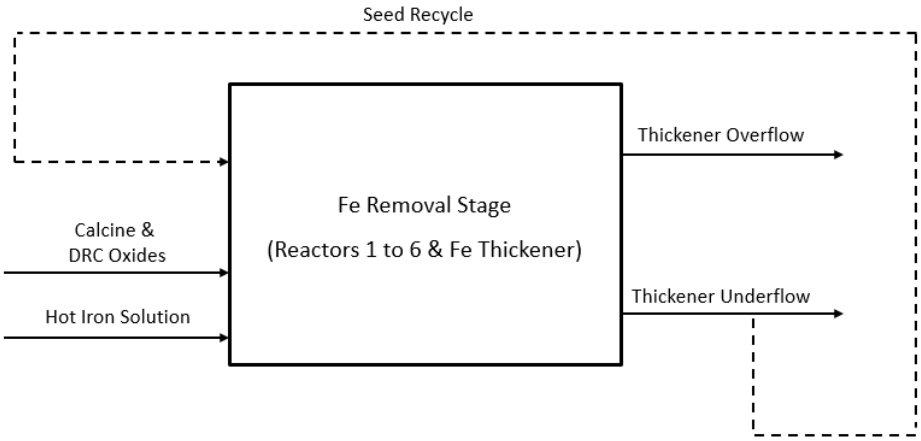


FIGURE 25: SCHEMATIC INDICATING THE INPUT AND EXIT STREAMS WITH THE SEED RECYCLE FOR THE MASS BALANCE

The equation shows that only the zinc in the input and exit streams need to be accounted for, while the zinc in the seed recycle can be disregarded. It must be noted here that this equation is only true for systems that are at operating at steady state.

In any mass balance there is a portion of zinc that cannot be accounted for. A number of factors contribute to the unaccounted zinc loss, but the majority of the unaccounted portion is likely to be attributed to the stream with the highest level of uncertainty. On the plant operation this stream was the thickener underflow, since the density and flowrate of this stream changed constantly, depending on the operational requirements of the thickener. The unaccountable zinc loss was calculated by subtracting the zinc in the exit streams from the zinc contained in the incoming streams. The same procedure was followed for the fluoride balance.

4.2. RESULTS & DISCUSSION:

4.2.1. OUTCOME OF MASS BALANCE:

The plant trial ran over a period of four weeks. No seed was added during the first week in order to establish a base case. The addition rate was increased weekly, until a solids build-up in the thickener resulted in the termination of the seeding programme. *Table 14* summarises the plant parameters and the results from the mass balance. The detailed mass balance can be found in *Appendix 3.*

The results and parameters in *Table 14* are represented graphically in *Figure 26*, *Figure 27*, *Figure 28*, *Figure 29* and *Figure 30*.

TABLE 14: SUMMARY OF PLANT PARAMETERS AND MASS BALANCE RESULTS FROM PLANT TRIAL (SEPT TO OCT 2011)

PARAMETERS:	27-Sep-11	30-Sep-11	1-Oct-11	2-Oct-11	5-Oct-11	6-Oct-11	7-Oct-11	8-Oct-11	9-Oct-11	11-Oct-11	12-Oct-11	13-Oct-11	14-Oct-11	15-Oct-11	17-Oct-11	18-Oct-11	19-Oct-11
SEED (m^3/hr)	0	0	0	0	1.92	1.92	1.92	1.92	1.92	3.83	3.83	3.83	3.83	3.83	5.75	5.75	5.75
Flowrate (m^3/hr)	53.5	61.7	61.0	59.9	66.2	66.4	53.3	60.8	55.7	65.0	63.8	52.8	60.8	62.6	65.2	76.1	64.2
Temp (^{0}C)	65	63	59	54	54	58	58	61	64	65	65	62	64	66	65	66	62
pH No. 1	3.21	3.22	3.33	3.17	3.12	3.16	3.16	3.22	3.26	3.33	3.19	3.35	3.19	3.20	3.12	3.10	3.12
pH No. 2	2.95	2.91	2.95	3.02	2.94	2.98	3.02	3.12	3.05	3.03	2.95	3.11	2.91	2.93	2.92	2.91	2.99
HIS Fe (g/l)	14.3	12.5	11.0	9.7	5.3	5.4	6.8	5.5	6.9	11.3	12.6	12.5	15.2	16.6	14.5	13.7	12.9
FS Zn (g/l)	20.2	23.9	26.2	26.8	33.2	34.1	20.1	23.5	21.2	25.2	22.0	20.6	16.6	20.4	26.2	32.0	26.4
Wash ratio	2.05	2.33	1.02	2.60	1.39	1.86	1.94	1.61	1.59	1.01	0.96	1.28	0.96	0.90	0.78	0.85	0.18
Residue volume (m^3)	26.79	24.94	26.73	19.75	18.58	14.54	14.57	15.88	17.35	29.42	30.57	30.64	31.68	32.32	38.20	36.91	36.18
RESULTS:	27-Sep-11	30-Sep-11	1-Oct-11	2-Oct-11	5-Oct-11	6-Oct-11	7-Oct-11	8-Oct-11	9-Oct-11	11-Oct-11	12-Oct-11	13-Oct-11	14-Oct-11	15-Oct-11	17-Oct-11	18-Oct-11	19-Oct-11
Zn Recovery (%)	91.27	91.65	90.05	90.04	88.84	89.31	88.25	90.16	89.13	91.18	91.11	91.36	93.20	93.00	93.13	93.54	91.63
Unaccounted (%)	11.54	14.19	11.56	6.09	11.87	12.16	1.24	7.50	4.35	14.58	15.83	17.79	13.93	11.11	10.92	10.10	13.70
Sol Zn losses (%)	1.43	1.30	1.14	0.98	0.90	0.82	0.81	0.92	0.93	1.14	1.20	1.13	1.17	1.11	1.54	1.59	1.40
Insol Zn losses (%)	7.30	7.05	8.81	8.99	10.26	9.87	10.93	8.91	9.94	7.68	7.69	7.51	5.64	5.89	5.33	4.87	6.97
F rejection (%)	94.93	93.68	94.30	94.75	86.85	89.10	87.33	86.92	89.94	88.76	87.91	87.91	87.76	88.54	89.00	86.59	87.20

The unaccounted loss was relatively high at an average of approximately 11 % for the duration of the plant trial. The biggest contributors to the unaccounted portion of zinc were believed to be the Iron Thickener underflow stream and the fact that the operation was not at steady state (refer to *Section 4.1.6*). This number was not considered excessive when compared to the average Zincor unaccounted loss of approximately 15 % (for the period of 1 January 2009 to 30 September 2011).

Figure 26 plots the soluble and insoluble losses overlapped with the seed recycle.

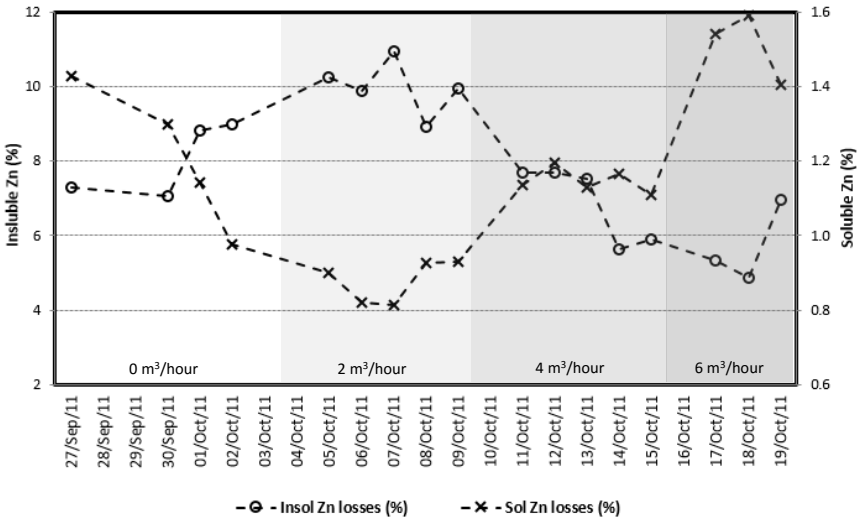


FIGURE 26: PLOT OF SOLUBLE AND INSOLUBLE ZINC LOSSES OVERLAPPED WITH SEED RECYCLE

The soluble loss initially decreased from 1.4 % to a minimum of 0.8 % at a seed recycle of 2 m^3/hr. The improvement may be attributed to agglomeration growth, which is promoted by the presence of seed [Lewis, 2009; Claassen, 2005]. A sharp increase was seen in the soluble zinc loss as the seed recycle was increased to 4 and 6 m^3/hr. The maximum soluble loss was between 1.4 and 1.6 % zinc. This trend may be attributed to the steady increase in the residue volume as the seed recycle volume was increased to the maximum set-point (refer to *Figure 27*). In fact, the residue volume almost doubled from approximately 18 to just under 40 m^3. The result was a decrease in the wash ratio. An increase in the wash water addition to accommodate for the additional solids reporting to the belt filter was not possible, due to high plant solution inventory during this period.

The seed recycle volume would impact on the residue volume only until the operation reaches steady state. The HIS iron content determines the amount of iron residue generated, with a high iron content giving a high residue volume. *Figure 28* shows that the HIS iron content and residue volume followed the same trend. The combination of an increase in the HIS iron content and the seed recycle rate contributed to the significant increase in residue volume.

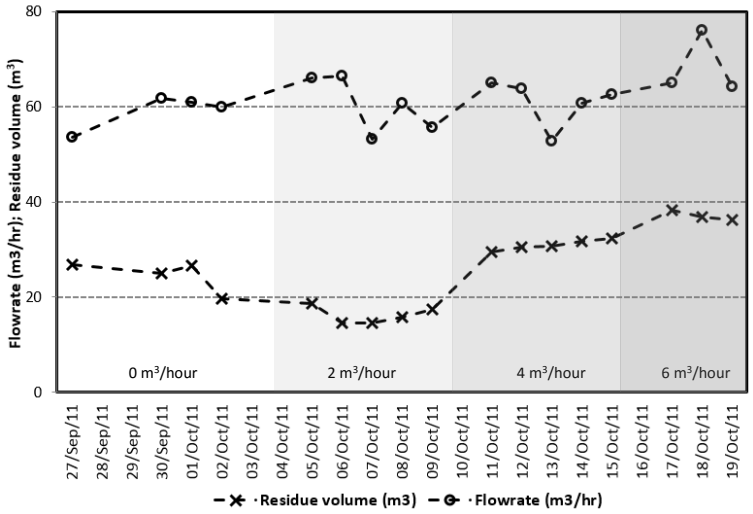


FIGURE 27: PLOT OF FLOWRATE AND RESIDUE VOLUME OVERLAPPED WITH SEED RECYCLE

The insoluble loss increased from 7 to 11 % during the first half of the plant trial (refer back to *Figure 26*). This could be explained by the general reduction in both residence time (indicated by an increase in the flowrate through the Iron Removal Stage seen in *Figure 29 (b)*) and the operating temperature (refer to *Figure 29 (a)*) during this period. Haegele *et al*. (1992a) found that an increase in operating temperature improves the efficiency of the precipitation reaction and a longer residence time supports the formation of a better quality residue.

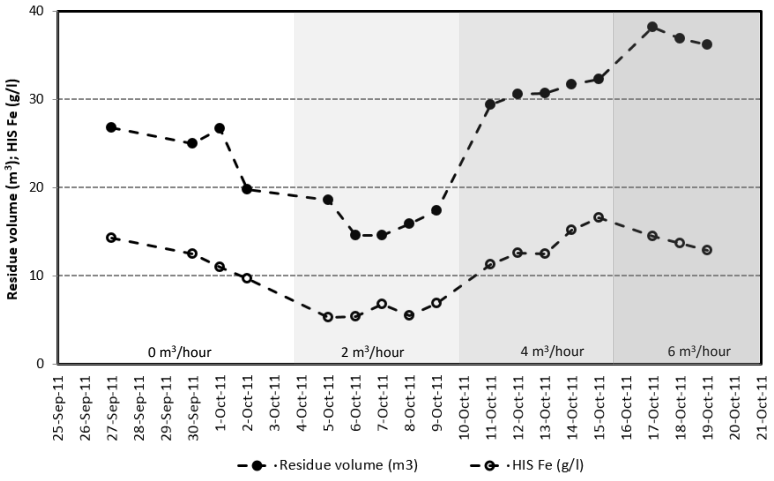


FIGURE 28: PLOT OF RESIDUE VOLUME OVERLAPPED WITH HIS Fe CONTENT

The insoluble zinc loss then decreased to between 5 and 6 % during the latter portion of the plant trial, where the seed recycle rate was increased to 4 and 6 m^3/hr. The reasons may be attributed to the general upward trend of the operating temperature from a low of approximately 55 to a high of 65 °C (refer to *Figure 29 (a)*). The data for the plant flowrate in *Figure 29 (b)* is quite erratic, but the overall trend showed a steady increase in the flowrate (from an average of approximately 55 to almost

65 m^3/hr) with an increase in the seed recycle. This equated to a decrease in the residence time across the Iron Removal Stage. This would typically be detrimental to the process, since an increase in residence time promotes agglomeration [Lewis, 2009; Claassen, 2005] and improves the quality of the residue [Haegele *et al.*, 1992a]. However, any negative impact that the lower residence time may have had on the operation was off-set by the increase in operating temperature and presence of seed (as evidenced by the downward trend in the insoluble zinc loss in the latter part of the plant trial). The presence of seed provides additional surface area for precipitation so that there is less coating of unleached neutralising agent by precipitate [Claassen, 2005]. The SEM images (refer to *Section 4.2.5*) appear to support this data.

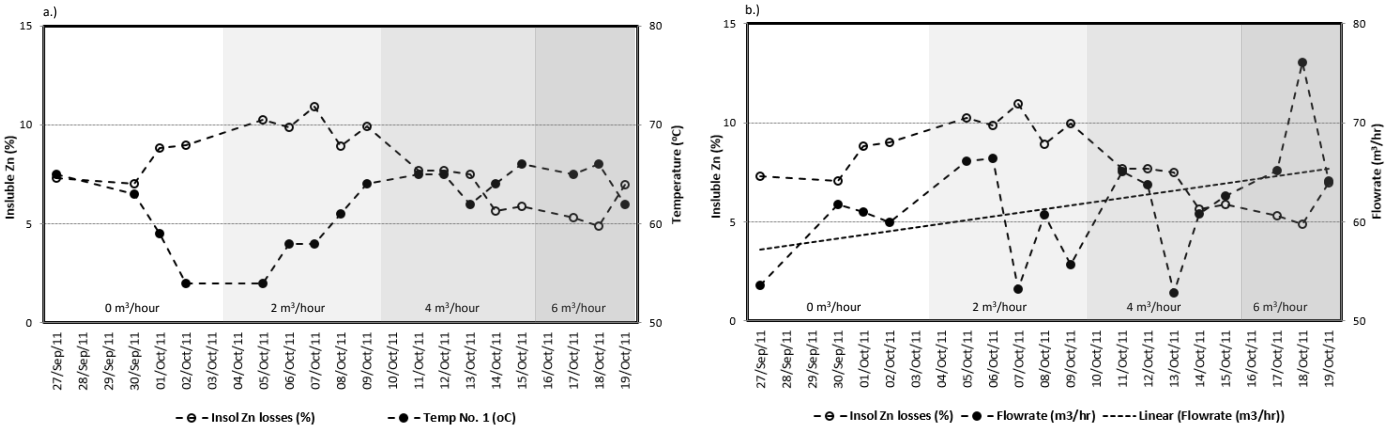


FIGURE 29: PLOT OF INSOLUBLE Zn LOSSES VERSUS TEMPERATURE a.) AND FLOWRATE b.) OVERLAPPED WITH SEED RECYCLE

The profile of the overall zinc recovery and the fluoride rejection can be seen in *Figure 30*. The results show that there was a general upward trend of the overall zinc recovery over the period of the plant trial. The improvement was attributed largely to the decrease in the insoluble portion of the zinc losses, since the soluble losses increased over the same period. This was particularly true for the latter half of the plant trial with high seed recycle volumes.

The amount of fluoride rejected appeared to decrease from approximately 95 % to between 85 and 90 % with an increase in the seed recycle rate. The reason for this was not clear, but may be related to the morphology of the precipitate. Claassen *et al*., 2002 and 2007 found that the Zincor precipitate contained phases that were poorly crystalline and contained high levels of impurities. Since seed addition promotes the formation of coarser and denser precipitate, the halide rejection rate may decline in the presence of seed.

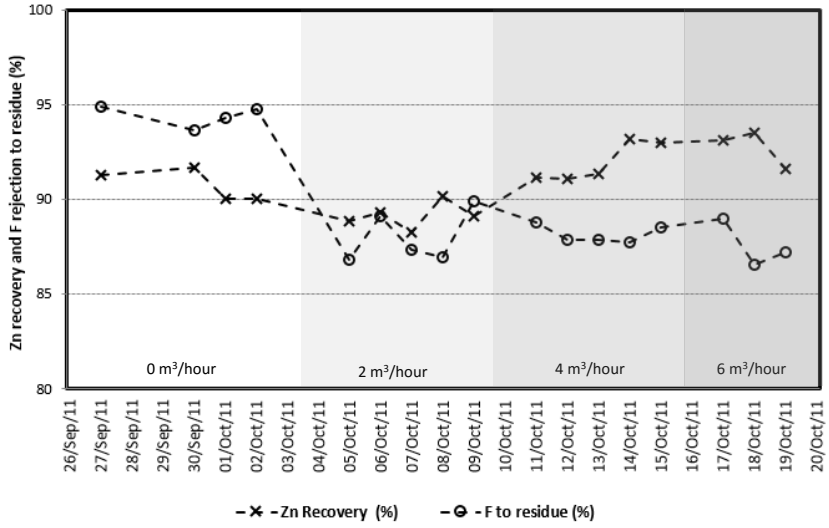


FIGURE 30: PLOT OF ZINC RECOVERY AND FLUORIDE REJECTION OVERLAPPED WITH SEED RECYCLE

The Literature Review (in particular *Section 2.3*) highlighted a number of key parameters for consideration during precipitation. These and other plant parameters were plotted against the soluble and insoluble zinc losses for the period of the plant trial to determine the correlation coefficient or 'goodness of fit'. A summary of the results is available in *Table 15*.

The Zincor operation was a complex and dynamic environment with multiple parameters changing constantly and simultaneously. While the use of the correlation coefficient as an analysis tool had limitations and could not be considered statistically significant or conclusive, it assisted in sorting and evaluating the results and aided in the discussions. Correlation between parameters did not necessarily imply causation and correlation could at times be attributed to a third parameter.

For the purposes of the following discussion, parameters with an R^2 of more than 0.5 were considered relatively significant to the process, particularly due to their impact on the zinc losses and ultimately the zinc recovery. Those with an R^2 of between 0.2 and 0.5 were considered less significant, but prominent enough to include in the discussion. Those with an R^2 of less than 0.2 were not included in the discussion.

From *Table 15*, the parameters that appeared to be more significant with regards to soluble zinc losses were temperature, the iron content of the HIS and the zinc content of the Final Solution. Slightly less prominent were seed recycle, the second reactor pH and the wash ratio.

TABLE 15: A SUMMARY OF THE CORRELATION COEFFICIENTS FOR THE INSOLUBLE AND SOLUBLE ZINC LOSSES VERSUS SELECTED PLANT PARAMETERS FOR THE PERIOD OF THE PLANT TRIAL (SEPTEMBER TO OCTOBER 2011)

PARAMETER	Sol Zn		Insol Zn	
	R^2	Relationship	R^2	Relationship
Seed (m^3)	0.22	D	0.35	I
Flowrate (m^3/hr)	0.13	D	0.17	I
Temp No. 1 (°C)			0.54	I
Temp thick O/F (°C)	0.5312	D		
pH (No. 1)	0.04	I	0.02	D
pH (No. 2)	0.26	I	0.24	D
HIS Fe (g/l)	0.61	D	0.80	I
HIS H_2SO_4 (g/l)	0.00	-	0.03	D
FS Zn (g/l)	0.62	D	0.79	I
wash ratio	0.21	I	0.27	D

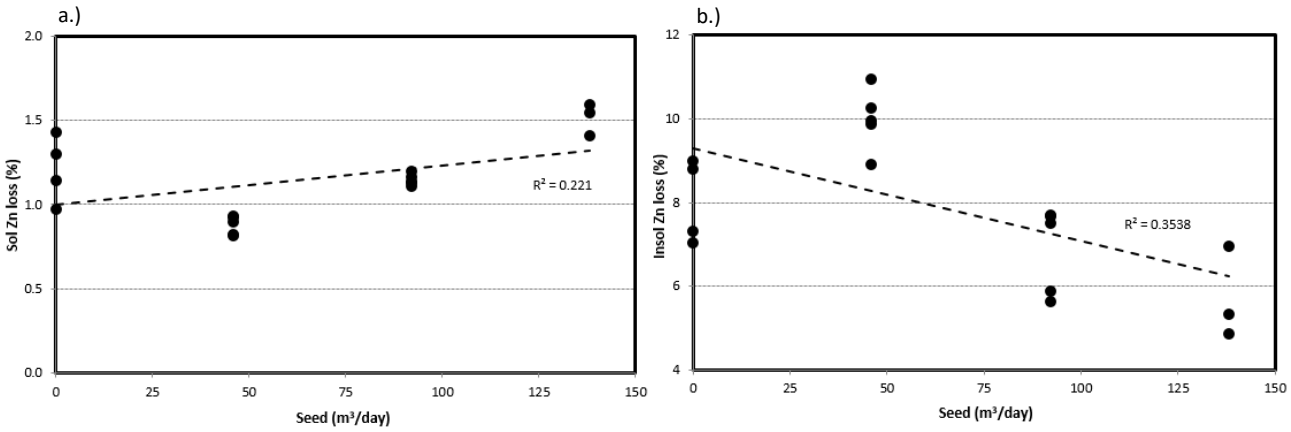
D – Directly proportional; I – Indirectly proportional

The prominent parameters in terms of the insoluble zinc loss were temperature, Hot Iron Solution (HIS) iron content and Final Solution zinc content. Slightly less prominent parameters were seed recycle, the second reactor pH and the wash ratio.

While some of these parameters have already been explored briefly in the preceding paragraphs, each parameter will now be looked at in isolation in the discussion that follows.

SEED:

The graphs of the soluble and insoluble zinc loss versus the seed addition are shown in *Figure 31*.



NOTE: Seed addition at 0, 46, 92 & 138 m^3 seed/day

FIGURE 31: PLOT OF SOLUBLE (a) AND INSOLUBLE (b) ZINC LOSS VERSUS TOTAL DAILY SEED ADDITION

The seed addition had a moderate and directly proportional correlation with the soluble zinc loss, so that the soluble zinc loss appeared to increase with an increase in the seed addition rate. This correlation was attributed to the increase seen in the residue volume with an increase in the seed addition for the duration of the plant trial (refer to *Figure 27*), which negatively impacted on the wash ratio. Ideally, the amount of wash water addition should have been increased to accommodate for the additional residue. The residue volume would reach a plateau once steady state was achieved.

The seed addition had a moderate and indirectly proportional correlation with the insoluble zinc loss. The presence of seed seemed to result in a decrease in the insoluble portion of the zinc loss, which was attributed to the additional surface area, or precipitation sites, provided by the seed [Claassen, 2005]. This finding was supported by the SEM images presented in *Section 4.2.5,* where there appeared to be less coating of neutralising agent in the precipitate produced at higher seed recycle volumes.

TEMPERATURE:

The graphs of soluble and insoluble zinc losses versus temperature are presented in *Figure 32*.

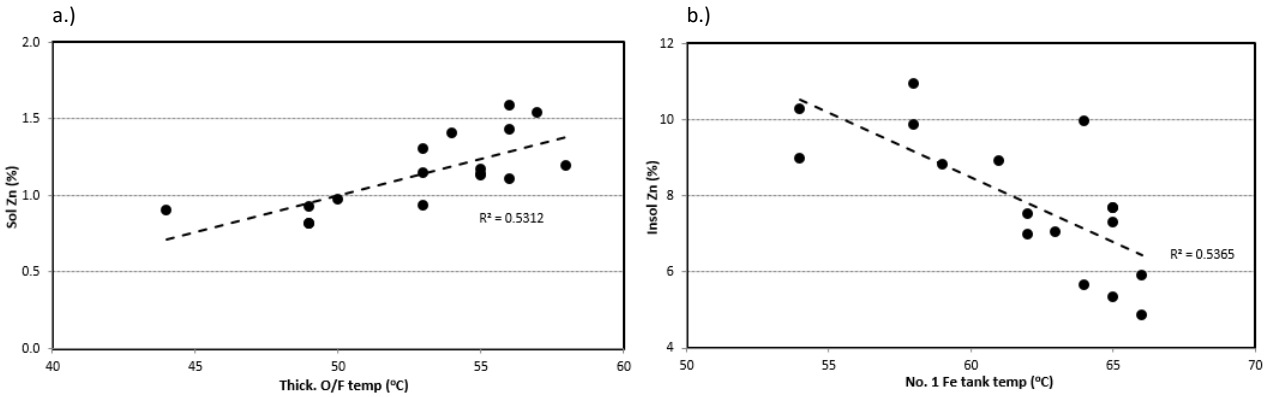


FIGURE 32: PLOT OF SOLUBLE (a) AND INSOLUBLE (b) ZINC LOSS VERSUS TEMPERATURE

The temperature used to plot the graph in *Figure 32 (a)* was that of the thickener overflow, since there was a decrease in temperature across the Iron Removal circuit of approximately 10 ^{o}C. The trend shows that temperature had a significant and directly proportional correlation with the soluble zinc loss, so that an increase in temperature would lead to an increase in the soluble zinc loss. However, an increase in operating temperature typically benefits filtration by increasing the rate of nucleation, crystal growth and agglomeration [Söhnel and Garside, 1993]. Since correlation does not always imply causation, a third parameter may be responsible for this trend. This parameter was believed to be the zinc content the Final Solution (iron thickener overflow) (refer to *Figure 33*).

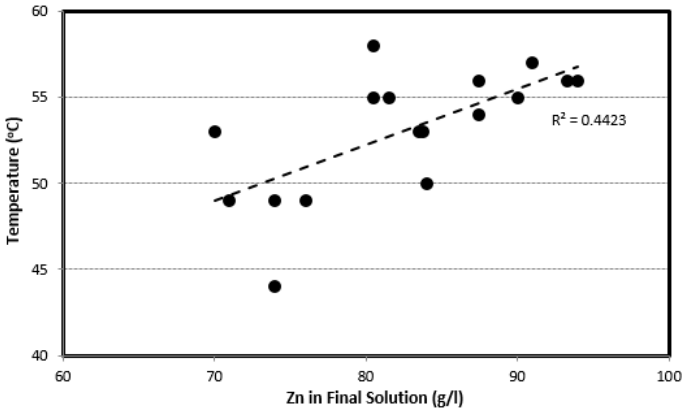


FIGURE 33: PLOT OF TEMPERATURE VERSUS THE FINAL SOLUTION Zn CONTENT

A relatively strong correlation existed between operating temperature and the Final Solution zinc content, with an increasing temperature leading to a higher solute concentration. This trend was probably as a result of an increase in the leaching efficiency of the zinc-rich neutralising agent with an increase in operating temperature. It was seen in *Section 2.3.7* that solution viscosity is a function of temperature, pressure and solution concentration. An increase in the solution concentration (in this case the zinc content of the Final Solution) leads to an increase in the solution viscosity, inhibiting particle settling in the thickener and negatively impacting on the soluble zinc loss.

The temperature used to plot the graph in *Figure 32 (b)* was that in the first iron removal reactor where heating was maintained with steam. The trend shows that temperature had a significant and indirectly proportional correlation with the insoluble zinc loss with an increasing operating temperature leading to a reduction in the insoluble portion of the zinc loss. Haegele *et al*., 1992a found that precipitation efficiency improves with an increase in temperature. Temperature also influences the insoluble loss through its impact on supersaturation [Claassen, 2005]. In addition, the leaching efficiency of zinc ferrites would improve at escalated temperatures, reducing the insoluble zinc loss.

ZINC CONTENT OF FINAL SOLUTION:

The graph of the soluble and insoluble zinc losses versus the Final Solution zinc content can be seen in *Figure 34*.

The trend in *Figure 34 (a)* shows that the Final Solution zinc content had a strong and directly proportional correlation with the soluble zinc loss, so that an increase in the solute concentration resulted in higher soluble zinc losses. An increase in solute concentration increases solution viscosity [Themelis, 1995], hindering particle settling in the thickener and contributing to elevated soluble zinc

losses. Dilution of the thickener feed and maximising the wash ratio on the belt filter may negate the negative effect of high solution viscosity.

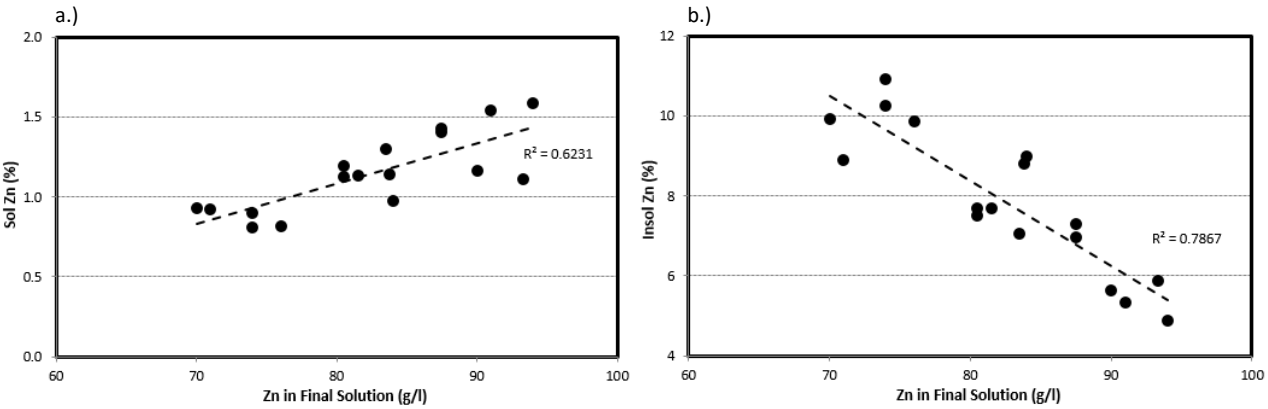


FIGURE 34: PLOT OF SOLUBLE (a) AND INSOLUBLE (b) ZINC LOSS VERSUS FINAL SOLUTION Zn CONTENT

Figure 34 (b) shows that the zinc content in the Final Solution had a strong and indirectly proportional correlation with the insoluble zinc loss, so that an increase in the solute concentration resulted in a lower insoluble zinc loss. To further examine this correlation a few other parameters were considered. *Figure 35* depicts the profiles of the Final Solution zinc content, the HIS iron content as well as the neutralising agent consumption for the duration of the plant trial. The neutralising agent consumption was considered in terms of zinc tonnes, since DRC oxide and calcine did not have the same zinc content.

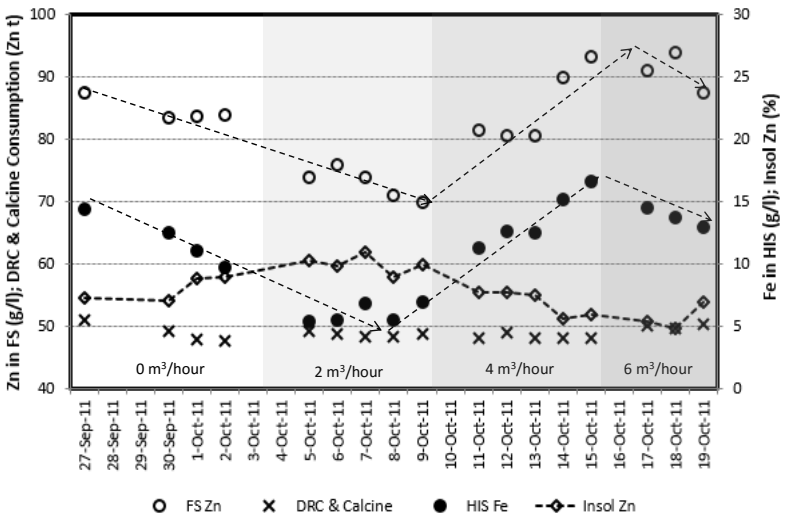


FIGURE 35: PROFILE OF ZINC IN FINAL SOLUTION, IRON IN HIS, NEUTRALISING AGENT CONSUMPTION AND INSOLUBLE Zn LOSS FOR THE DURATION OF THE PLANT TRIAL

The neutralising agent consumption remained relatively constant for the duration of the plant trial with a narrow range of 48 to 51 zinc tonnes. This was as a result of the way the process was operated. The two neutralising agents were fed at a constant rate, while the HIS addition rate was automatically controlled to maintain the slurry pH.

Both the Final Solution zinc content and the HIS iron content followed the same trend, while the insoluble zinc loss appeared to have the opposite trend. In other words, as the solution concentrations decreased during the first portion of the plant trial the insoluble zinc loss gradually increased to a maximum of 11 %. As these solution concentrations increased during the second half of the trial the insoluble zinc loss decreased to between 5 and 6 %. The one parameter that these trends had in common was the operating temperature (refer to *Figure 29 (a)*, *Figure 32* and *Figure 36*). An increase in operating temperature improves precipitation efficiency [Haegele *et al*., 1992a] and influences the insoluble loss through its impact on supersaturation [Claassen, 2005].

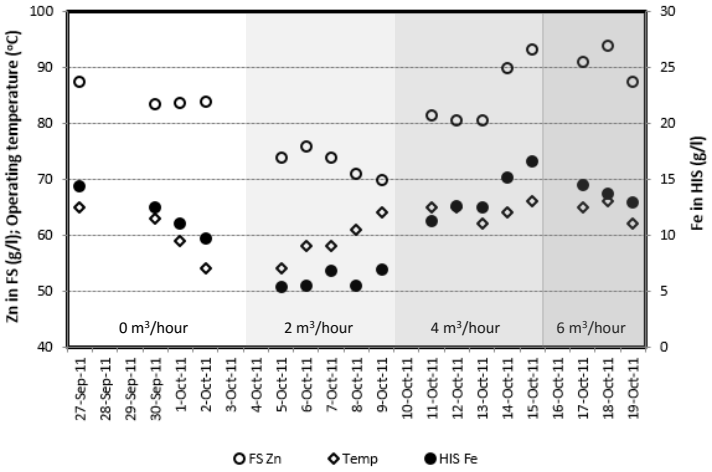


FIGURE 36: PROFILE OF FINAL SOLUTION ZINC CONTENT, HIS IRON CONTENT AND OPERATING TEMPERATURE FOR THE DURATION OF THE PLANT TRIAL

With so many parameters changing simultaneously it was difficult to determine whether, or to what extent, the presence of seed contributed to the decrease seen in the insoluble zinc loss. The general downward trend in the insoluble zinc loss during the latter half of the plant trial also corresponded with the higher seed recycle rates of 4 and 6 m^3/hr.

No. 2 TANK pH:

Interestingly, the correlation between the first reactor pH and the zinc losses was insignificant (refer back to *Table 15*). It would appear that the pH in the second reactor, where the acid wash was

performed, was a far more critical parameter. The purpose of the acid wash was discussed in *Section 1.2.2*. The graphs of soluble and insoluble zinc losses versus the second reactor pH can be seen in *Figure 37*.

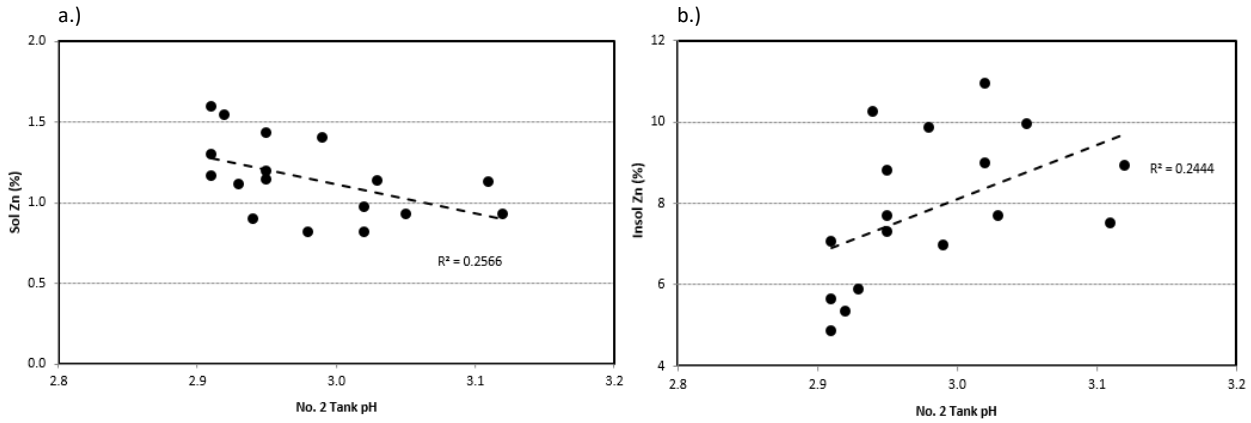


FIGURE 37: PLOT OF SOLUBLE (a) AND INSOLUBLE ZINC LOSS (b) VERSUS THE pH IN THE NO. 2 REACTOR

Figure 37 (a) indicates that a strong and directly proportional correlation existed between the pH and the soluble zinc loss, with an increasing pH profile leading to a reduction in the soluble zinc loss. This may have something to do with silica gel formation at a lower pH profile, which makes filtration of the precipitate very difficult.

The trend in *Figure 37 (b)* shows a strong and directly proportional correlation between the pH and the insoluble zinc loss. The main purpose of the acid wash was zinc recovery. A lower pH would recover more zinc and reduce the insoluble zinc loss.

There appeared to be an ideal operating window for the acid wash, since a high pH was favoured to minimise the soluble zinc loss and a low pH was favoured to minimise the insoluble zinc loss. Further work will be required in order to more accurately identify the optimal pH profile. The Zincor process operated at a pH of 3.2 in the first reactor and a pH of 3 in the acid wash step.

IRON CONTENT OF HIS:

The graphs of the soluble and insoluble zinc losses versus the HIS iron content are shown in *Figure 38*.

Figure 38 (a) shows that the HIS iron content had a strong and directly proportional relationship with the soluble zinc loss, so that an increase in the solute concentration resulted in an increase in the soluble zinc loss. However, a high HIS iron content is typically beneficial to the process, since the iron

contained in the HIS provides the cement needed for the precipitation reaction and supports agglomeration growth [Claassen and Sandenbergh, 2006]. Therefore, this correlation may have been the result of a third parameter, namely the Final Solution zinc content. The HIS iron content and Final Solution zinc content followed pretty much the same profile for the duration of the plant trial (refer back to *Figure 36*) and the two parameters have a very strong correlation (see *Figure 39*). It was seen in the preceding paragraphs that the solute concentration (Final Solution zinc content) strongly influenced the soluble zinc loss (also refer back to *Figure 34 (a)*) through its impact on the solution viscosity. An increase in the solute concentration leads to an increase in the solution viscosity [Themelis, 1995], which negatively impacts the settling and filtration of the precipitate, hence increasing the soluble portion of the zinc losses.

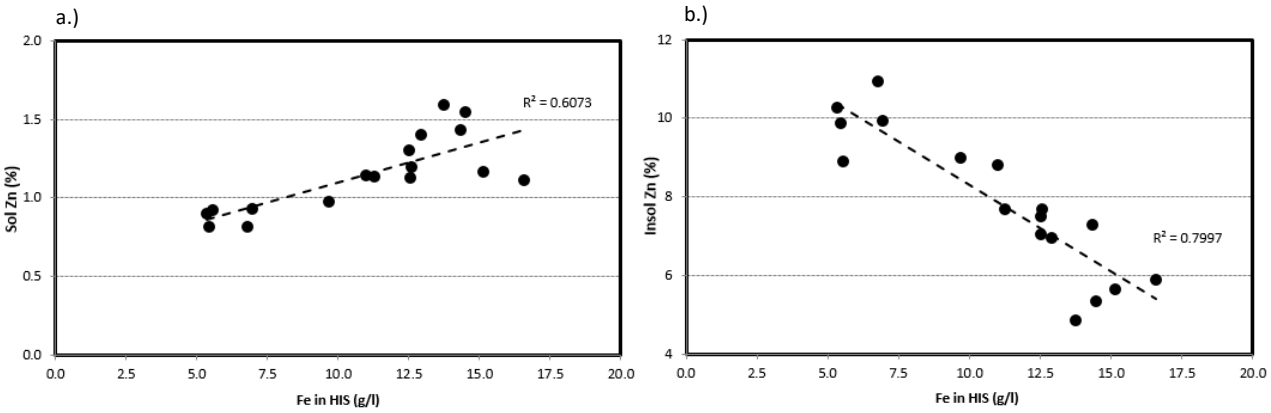


FIGURE 38: PLOT OF SOLUBLE (a) AND INSOLUBLE (b) ZINC LOSS VERSUS THE HIS Fe CONTENT

Figure 38 (b) shows that the HIS iron content had a strong and inversely proportional correlation with the insoluble portion of the zinc loss, meaning that an increase in the iron content resulted in a decrease in the insoluble losses. This correlation can most likely be attributed to the operating temperature. The HIS iron content had a strong and directly proportional correlation with the operating temperature (see *Figure 40* and also refer back to *Figure 36*). Haegele *et al*. (1992a) found that precipitation efficiency increases at elevated temperatures. One should also see an improvement in the leaching efficiency of zinc ferrites at higher operating temperatures.

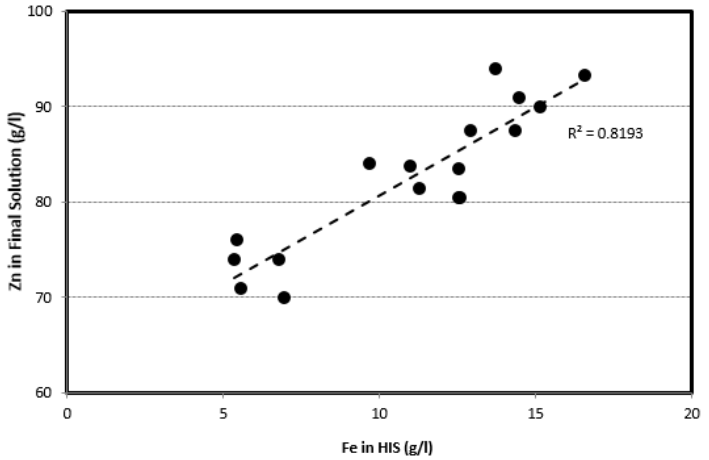


FIGURE 39: PLOT OF THE FINAL SOLUTION ZINC CONTENT VERSUS THE HIS IRON CONTENT

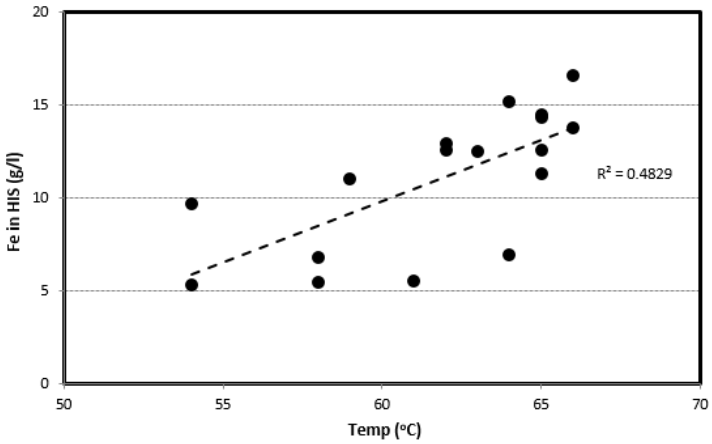


FIGURE 40: PLOT OF THE IRON CONTENT IN HIS VERSUS OPERATING TEMPERATURE

WASH RATIO:

The graphs of the soluble and insoluble zinc losses versus the wash ratio are depicted in *Figure 41.*

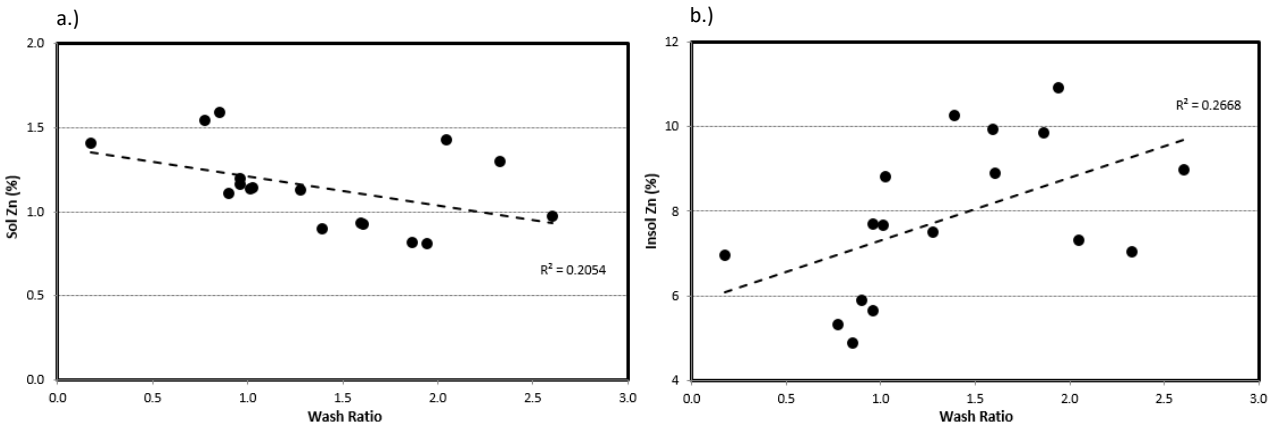


FIGURE 41: PLOT OF SOLUBLE (a) AND INSOLUBLE (b) ZINC LOSS VERSUS WASH RATIO

Figure 41 (a) shows that the wash ratio had a moderately strong and indirectly proportional correlation with the soluble zinc loss. Increasing the wash ratio (either by increasing the wash water addition or the filter area) should decrease the soluble zinc loss. The graph appears to indicate that a wash ratio in excess of 2 should be sufficient to maintain the soluble zinc loss below 1 %. This number was supported by Claassen *et al.*, (2002) who found that the soluble zinc loss could be maintained at or below an average of 1% at a wash ratio of 2.1 on the Zincor vacuum belt filters.

Figure 41 (b) shows that the wash ratio had a moderately strong and directly proportional correlation with the insoluble zinc loss. Wash ratio has no impact on the insoluble zinc loss and is largely influenced by the amount of residue reporting to the belt. The residue volume was determined by the HIS iron content and the seed recycle volume. *Figure 42* depicts the profiles of the residue volume, wash ratio and HIS iron concentration for the duration of the plant trial.

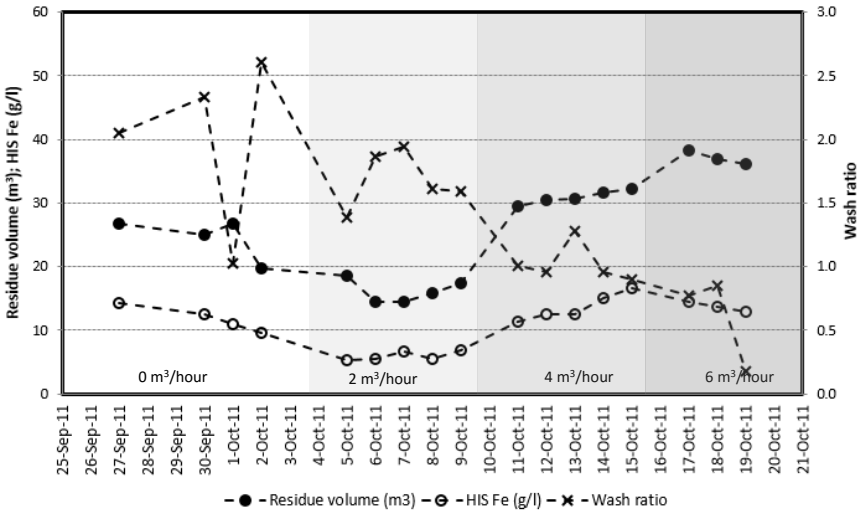


FIGURE 42: PROFILE OF RESIDUE VOLUME, HIS Fe CONTENT AND WASH RATIO OVERLAPPED WITH SEED RECYCLE

The residue volume and HIS iron content followed the same trend, since a higher iron content in the HIS generate more iron residue (also refer back to *Figure 28*). Both these parameters showed a steady increase over the period of the plant trial, while the wash ratio showed a dramatic decrease from above 2 to below 0.5. The preceding discussions showed that the operating temperature strongly influenced the HIS iron content and therefore the insoluble zinc loss (refer back to *Figure 36*, *Figure 38* and *Figure 40*). It was also noted that the presence of seed (particularly at a recycle volume of 4 and 6 m^3/hr) correlated with the downward trend in the insoluble zinc loss.

4.2.2. OUTCOME OF PSD ANALYSES:

Slurry samples were taken daily from the first, second, fourth and sixth reactors. A Malvern Particle Size Analyser was used to determine the particle size distribution of the solids. The D_{10}, D_{50} and D_{90} for each of the samples are represented graphically in *Figure 43*, *Figure 44* and *Figure 45*.

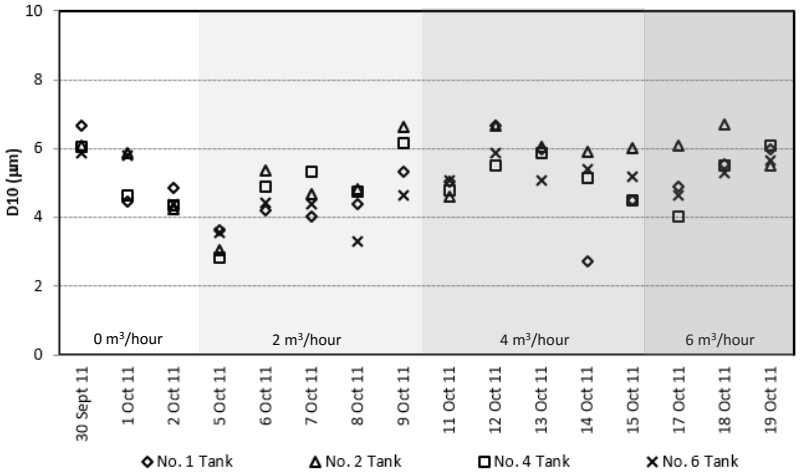


FIGURE 43: PLOT OF 10% PASSING FOR REACTORS NO. 1, 2, 4 AND 6

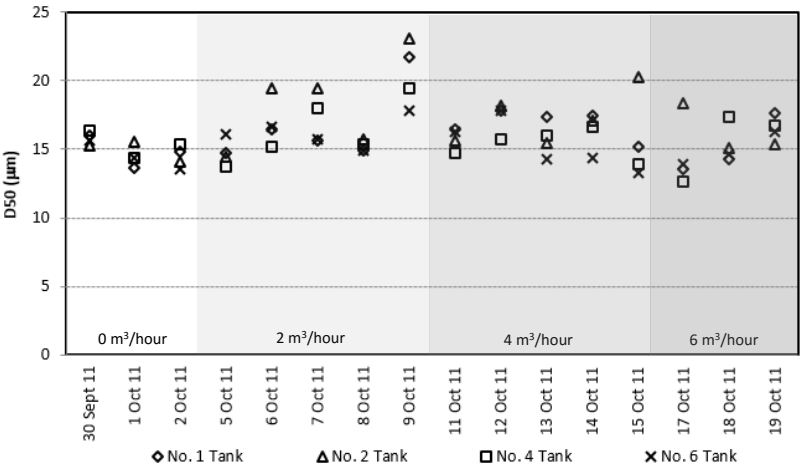


FIGURE 44: PLOT OF 50% PASSING FOR REACTOR NO. 1, 2, 4 AND 6

The data was scattered, so that it was difficult to determine a trend. However, the following observations could be made:

- In both *Figure 43* and *Figure 44* the particles were the largest in the second reactor, while those in the fourth and sixth reactors were the smallest. It appeared that particles increased in size only to decrease again, possibly due to attrition. A similar trend was seen in the laboratory work (refer to *Figure 17* in *Section 3.2.1.1*.).

- *Figure 44* showed some increase in particle size between the 'no seed' and '2 m^3/hr seed' scenarios, indicated by the gradual upward trend in the first two weeks of the trial. This was followed by a slight decrease in the particle size at 4 and 6 m^3/hr seed recycle rates. While seed addition (in the presence of Fe) promotes agglomeration growth [Lewis, 2009; Claassen, 2005], these particles need time to grow [Söhnel and Garside, 1993]. A seed recycle at the expense of residence time may be counter-productive.
- *Figure 45* showed the same trend, with an increase in particle size between the 'no seed' and '2 m^3/hr seed' scenarios, followed by a decline in particle size at a seed recycle rate of 4 m^3/hr. There seemed to be a second increase in particle size at the maximum seed addition rate of 6 m^3/hr, where the biggest particles were present in the last two reactors. This hints at the importance of residence time in agglomeration growth. The presence of seed appeared to have the biggest impact in the larger size fractions.

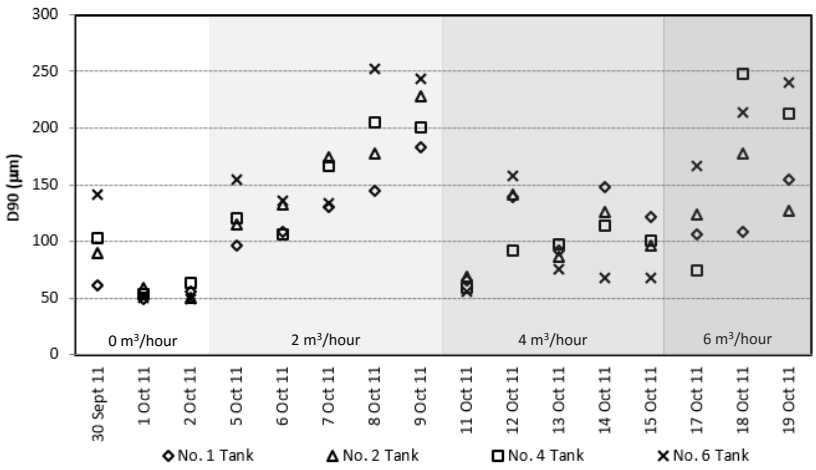


FIGURE 45: PLOT OF 90% PASSING FOR REACTORS NO. 1, 2, 4 AND 6

Particles of below 10 μm in size are conventionally classified as 'fines'. This size fraction complicates the dewatering and materials handling of a precipitate. *Figure 46* represents the fraction below 10 μm in size for samples from reactors 1, 2, 4 and 6 for the 'no seed', 2 m^3/hr seed, 4 m^3/hr seed and 6 m^3/hr seed scenarios.

The largest portion of fines appeared in the fourth and sixth reactors, which may have been the result of attrition. The steady increase in the solids loading across the Iron Removal circuit with an increase in the seed recycle rate (refer back to *Table 14*) hinted at the possibility of particle crowding. Particle crowding negatively impacts agglomeration growth through dis-agglomeration [Claassen and Sandenbergh, 2006].

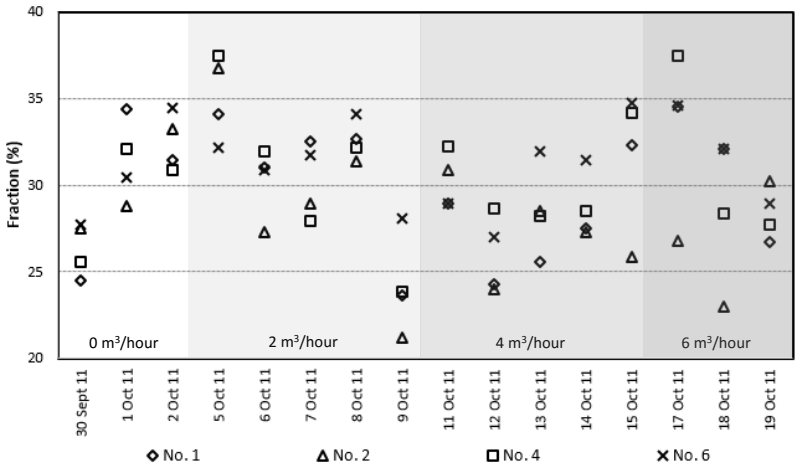


FIGURE 46: THE FRACTION OF THE SAMPLE BELOW 10 μm FOR REACTORS NO. 1, 2, 4 AND 6

4.2.3. OUTCOME OF SETTLING TESTS:

Settling tests were performed daily on samples from the thickener feed. The results are presented graphically in *Figure 47*.

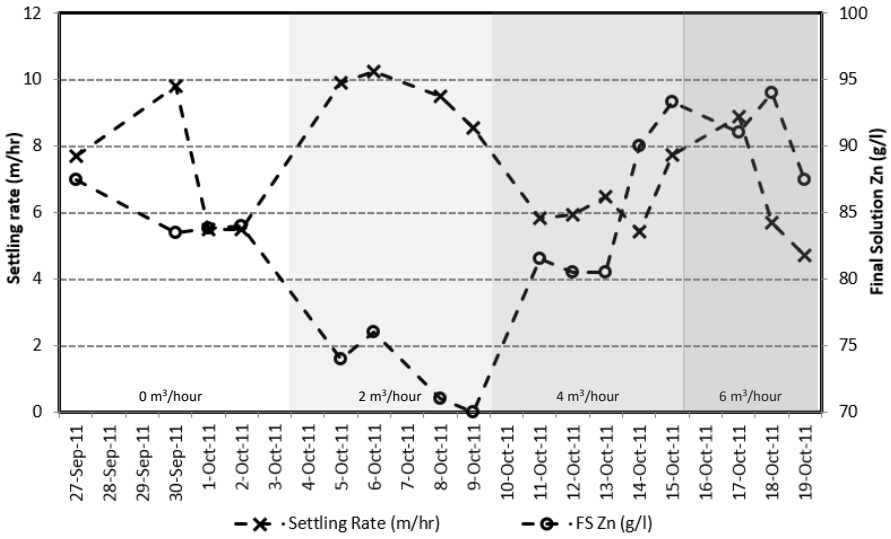


FIGURE 47: PLOT OF SETTLING RATE AND FINAL SOLUTION Zn CONTENT OVERLAPPED WITH THE SEED VOLUME

There was an increase in the settling rate between the 'no seed' and '2 m^3/hr seed' scenarios. The presence of seed promotes agglomeration growth and improves settling [Lewis, 2009; Claassen, 2005]. This was confirmed by the PSD results discussed in *Section 4.2.2*, which showed an increase in the particle size with the implementation of a seed recycle (refer to *Figure 44* and *Figure 45*). There was a general downward trend in the settling rate as the seed recycle rate was increased to 4 and 6 m^3/hr. This may be attributed to particle crowding, which hinders settling. This was supported by the

increase in the residue volume from 20 to 40 m^3 per day over the period of the plant trial (refer to *Table 14* and *Figure 27*).

The settling rates appeared to be higher when the Final Solution zinc concentration was low. Viscosity is a function of solute concentration (refer to *Section 2.3.7*), with an increase in solution concentration resulting in a higher solution viscosity. A high solution viscosity restricts the ease at which particles move in liquor, resulting in poor settling and filtration (and ultimately high soluble zinc losses).

The Final Solution zinc content increased dramatically from 70 to just over 90 g/l in the latter half of the plant trial. This had a significant impact on the solution viscosity and particle settling in the thickener. The reason for this increase was discussed in *Section 4.2.1*, but had to do with the HIS iron content and the operating temperature (refer to *Figure 34* and *Figure 35*).

Figure 48 plots the cake moisture, residue volume, wash ratio and soluble zinc loss overlapped with the seed recycle rate. The cake moisture showed a steady decline over the period of the plant trial as the seed addition rate was increased. This was a good sign and implied that the presence of seed had had the desired outcome. However, the residue volume showed a steady increase (reasons for this were discussed in *Section 4.2.1*) while the wash ratio declined significantly (from approximately 2 to below 0.5). Wash water addition needs to accommodate for the increase in the residue volume in order to benefit from the presence of seed.

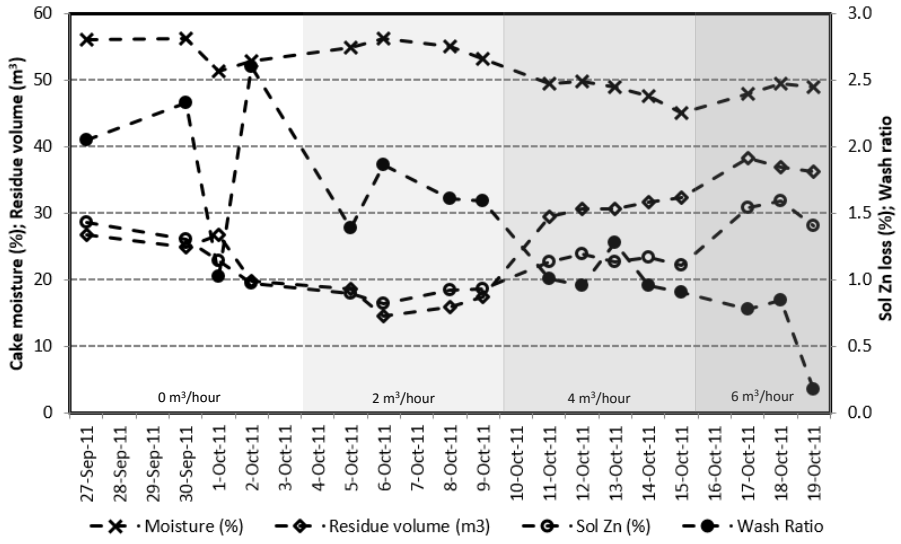


FIGURE 48: PLOT OF CAKE MOISTURE, RESIDUE VOLUME, WASH RATIO AND SOLUBLE ZINC LOSS

The work had to be terminated on the third day of operating at a 6 m^3/hr seed addition rate, due to a solids build-up in the iron thickener. This addition rate appeared to be excessive.

4.2.4. OUTCOME OF XRD ANALYSES:

A daily iron residue sample was submitted for XRD analyses. *Table 16* summarises these results.

TABLE 16: SUMMARY OF XRD RESULTS OF THE DAILY IRON RESIDUE SAMPLES

	1-Oct-11	2-Oct-11	3-Oct-11	4-Oct-11	5-Oct-11	6-Oct-11	7-Oct-11	8-Oct-11
SEED (m^3/hr)	0	0	0	2	2	2	2	2
Anglesite - $PbSO_4$ (%)	20.68	21.74	24.60	29.61	30.27	27.21	26.06	20.69
Bassanite - $CaSO_40.5H_2O$(%)	2.88	1.75		4.77		6.21		
Gypsum - $CaSO_4{\cdot}2H_2O$ (%)								
Hydrocalcite - $CaCO_3(H_2O)$ (%)								
Plumbo-jarosite - $PbFe_6(SO_4)_4(OH)_{12}$ (%)							1.57	3.45
Magnetite - Fe_3O_4 (%)	58.00	55.87	55.30	48.50	54.87	53.34	55.97	66.76
Quartz - SiO_2 (%)			6.74					
Sphalerite - ZnS (%)	0.71	1.55	2.31	2.00	1.93	4.39	3.77	
Willemite - Zn_2SiO_4 (%)	11.19	11.51	11.05	9.42	9.83	6.56	8.98	9.10
Zincite - ZnO (%)	6.54	7.58		5.71	3.10	2.28	3.65	

	9-Oct-11	11-Oct-11	12-Oct-11	13-Oct-11	14-Oct-11	15-Oct-11	17-Oct-11	18-Oct-11	19-Oct-11
SEED (m^3/hr)	2	4	4	4	4	4	6	6	6
Anglesite - $PbSO_4$ (%)	14.25	8.47	9.24	1.86	5.80	7.80	7.63	5.18	6.81
Bassanite - $CaSO_40.5H_2O$(%)								0.74	
Gypsum - $CaSO_4{\cdot}2H_2O$ (%)	5.40								
Hydrocalcite - $CaCO_3(H_2O)$ (%)					5.76	6.65			
Plumbo-jarosite - $PbFe_6(SO_4)_4(OH)_{12}$ (%)	6.73	22.62	26.81	46.30	33.34	31.75	48.39	52.38	48.22
Magnetite - Fe_3O_4 (%)	60.53	56.06	50.69	41.40	48.30	44.63	41.70	36.75	40.80
Quartz - SiO_2 (%)	5.85		4.02	3.20		3.14			
Sphalerite - ZnS (%)							2.28		
Willemite - Zn_2SiO_4 (%)	7.26	12.86	7.49	5.09	6.80	6.03		2.37	4.17
Zincite - ZnO (%)			1.75	2.15				2.58	

Claassen, 2002 found the presence of Schwertmannite, Ferrihydrite, Jarosite, Franklinite and an unknown poorly crystalline phase in the Zincor iron residue. He used only calcine as a neutralising agent. The use of DRC oxide as a supplement to calcine and the presence of seed in this study appeared to result in the formation of completely different complexes.

The following observations could be made regarding the results:

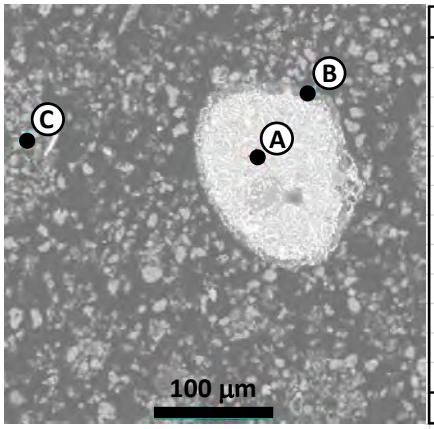
- The majority of the precipitate was identified as Magnetite. Since the formation of magnetite was not thermodynamically possible under these operating conditions (refer back to *Figure 6*) this complex was more likely to be Ferrihydrite;
- The other major complex was identified as Anglesite, which is a lead sulphate mineral. Its presence seemed to steadily decline as the seed recycle rate was increased;
- The Jarosite was identified as a Plumbo-Jarosite, due to the presence of lead in the circuit. The Jarosite was only present in the latter part of the plant trial and appeared to increase dramatically with an increase in the seed recycle rate;

- Due to incomplete roasting the calcine contained small amounts of Sphalerite. Its presence in the iron residue indicated coating of unleached calcine by iron precipitate. Except for one day, no Sphalerite was identified in the residue samples from the latter part of the plant trial. This supported the notion that seed reduces coating of unleached neutralising agent by providing additional surface area for precipitation;
- Zincite is the mineral form of zinc oxide and was present in small amounts, particularly in the first half of the trial. In the latter portion of the trial (at seed recycle rates of 4 and 6 m^3/hr) there were only a few days where Zincite was identified in the precipitate sample. As in the case of Sphalerite, this finding appeared to support the notion of seed reducing coating of unleached neutralising agent by iron precipitate.

4.2.5. OUTCOME OF SEM ANALYSES:

Figure 49, *Figure 50*, *Figure 51* and *Figure 52* are SEM images of iron residue samples at no seed, 2, 4 and 6 m^3/hr seed recycle rates. While SEM images can be subjective, a few observations were made.

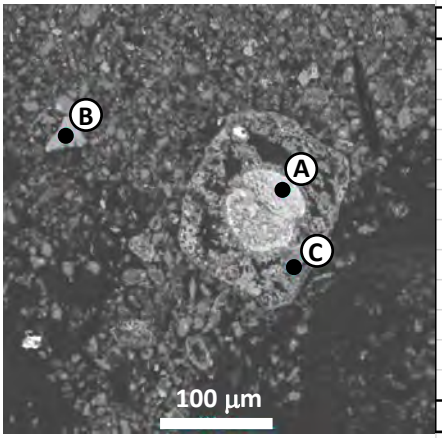
Figure 49 is an image of a precipitate sample taken when no seed was being added. Point 'a', an almost pure oxide particle (attributed to the high Zn and Pb content), was coated with a thin layer of iron precipitate (indicated by point 'b'). The presence of unleached zinc-rich neutralising agents in the iron residue contributed to the insoluble zinc losses.



Element	A (Wt %):	B (Wt %):	C (Wt %):
Zn	82.7	23.5	7.4
Fe	2.9	23	52.2
S	1.4	5.2	2.4
Pb	11.2	28.4	12.1
Cu	0.1	9.2	0.9
Al	0.4	6.4	3.8
Mn	0.3	0.3	0.1
Mg	0	0	0.1
Ca	0.1	0.2	2.8
Si	0.9	3.5	10.1
K	0.1	0	0.3
Ba	0	0.3	7.7
Total	**100.1**	**100**	**99.9**

FIGURE 49: SEM IMAGE OF IRON RESIDUE AT NO SEED RECYCLE

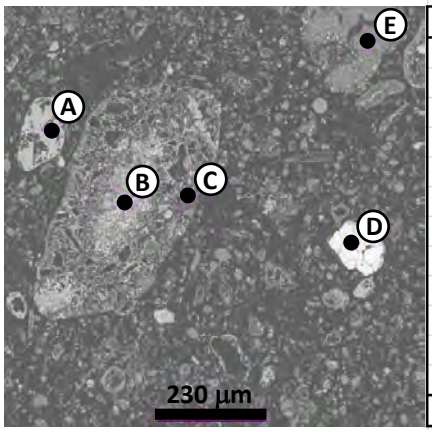
Figure 50 is an image of a precipitate sample taken at a seed recycle rate of 2 m^3/hr. Point 'a' was likely partially leached zinc oxide (due to the high Zn and Pb content) with an iron precipitate coating (indicated by point 'c').



Element	A (Wt %):	B (Wt %):	C (Wt %):
Zn	86.5	31.3	36.4
Fe	6.9	56	33.8
S	0.1	0.2	2.1
Pb	2.6	2.7	8.6
Cu	1.4	2.7	1.8
Al	0.5	0.4	3
Mn	1.4	6	5.8
Mg	0	0.3	0
Ca	0	0.1	0.2
Si	0.5	0.3	5.8
K	0	0	0
Ba	0	0	2.5
Total	99.9	100	100

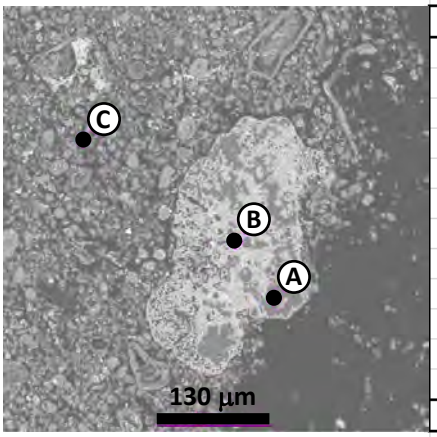
FIGURE 50: SEM IMAGE OF IRON RESIDUE AT 2m³/HR SEED RECYCLE

Figure 51 shows a precipitate sample taken at a 4 m³/hr seed recycle rate. Point 'b' appeared to be partially leached neutralising agent (attributed to the high Zn content) with an iron precipitate coating (refer to point 'c'). Point 'd' could be lead sulphate. The lead originated from the DRC oxide, which had a lead content of approximately 9 % for the period of 1 January 2009 to 30 September 2011.



Element	A (Wt %):	B (Wt %):	C (Wt %):	D (Wt %):	E (Wt %):
Zn	33.6	73.7	35.9	1.1	12.6
Fe	51.4	15.8	47.3	2	9.8
S	0.5	4.2	1.5	13.6	11.1
Pb	3.7	1.3	3.9	61.5	37.8
Cu	2.5	2.3	2.6	0.2	1.8
Al	0.1	0.5	2.4	0.1	0.1
Mn	7.2	1.1	3.2	0.4	10.4
Mg	0	0	0	0	0
Ca	0	0.1	0	1.5	13.4
Si	0.4	0.7	2.7	0.2	0.4
K	0	0	0.1	0.1	0
Ba	0.5	0.3	0.4	19.3	2.6
Total	99.9	100	100	100	100

FIGURE 51: SEM IMAGE OF IRON RESIDUE AT 4m³/HR SEED RECYCLE



Element	A (Wt %):	B (Wt %):	C (Wt %):
Zn	5	20.7	11.1
Fe	2.6	33.5	60.1
S	0.2	3.8	8.5
Pb	2.8	30.7	10.4
Cu	1.7	1.3	2.1
Al	0.3	0.3	1.8
Mn	0.6	6.1	0.6
Mg	0.3	0	0.1
Ca	0.1	0.3	0.3
Si	86	0.4	3.9
K	0	0	0.7
Ba	0.4	2.8	0.3
Total	100	99.9	99.9

FIGURE 52: SEM IMAGE OF IRON RESIDUE AT 6m³/HR SEED RECYCLE

Figure 52 shows a precipitate sample taken at a seed recycle rate of 6 m^3/hr. The large particle in the image did not show any evidence of coating. The darker areas in the particle (refer to point 'a') appeared to consist mostly of silica. The lighter areas (indicated by point 'b') consisted mostly of Fe, Zn and Pb.

A visual comparison of the precipitate samples taken at the different seed recycle rates appeared to show that coating of unleached neutralising agent by precipitate decreased in the presence of seed. These observations also supported the findings in the mass balance that showed a decrease in the insoluble zinc loss as the seed recycle rate was increased (refer back to *Table 14*).

5. CONCLUSIONS

Due to the limitations of the experimental procedure followed in the laboratory work and the fact that the operation never reached steady state during the plant trial, the outcomes of the work were not conclusive. However, the results from the various analyses appeared to support the hypothesis, so that some tentative conclusions could be drawn.

5.1. LABORATORY WORK:

5.1.1. PRELIMINARY LABORATORY WORK:

The tentative results appeared to show that seed is beneficial to the process by reducing the zinc losses. The zinc recovery improved from 90.12 % to an average of 93.31 % in the presence of seed.

The soluble zinc loss showed a decrease from 0.49 to an average of 0.17 %. The improvement was attributed to the presence of seed, which promoted agglomeration growth and improved the settling and filtration characteristics of the precipitate. This observation was supported by an increase in the precipitate particle size, particularly in the coarse size fraction in the final reactors.

The insoluble zinc loss decreased from 9.39 % to an average of 6.52 %. The improvement was credited to the additional surface area provided by the seed, resulting in less coating of zinc-rich neutralising agent by iron precipitate.

The final portion of this work evaluated alternative neutralising agents according to a number of selection criteria. The DRC oxide and limestone were deemed most suitable for further evaluation.

5.1.2. FINAL LABORATORY WORK:

Using limestone for neutralisation gave the lowest zinc recovery at 95.10 %. The soluble zinc loss made up the biggest portion of the losses at 3.66 %. This poor performance was attributed to the large volume of gypsum generated in the use of limestone for neutralisation. Since the wash water addition was not increased to accommodate for the additional residue volume, the wash ratio was negatively affected. In addition, it appeared that the precipitate was very fine and amorphous in nature, with poor settling and filtration characteristics. This theory was supported by the outcome of the settling tests, the particle size distribution and the XRD and SEM analyses performed on the precipitate. This

precipitate had the lowest settling rate of all the scenarios at 0.76 and 1.06 m/hr (at the two polymer dosages). The precipitate was very fine, with a D_{50} of 13 μm and a D_{90} of 30 μm. XRD analyses found that the precipitate was made up of mostly bassanite, which is an extremely fine gypsum-like compound. Finally, the SEM images showed the precipitate to be amorphous in nature. Amorphous particles typically retain zinc-rich liquor, contributing to the high soluble zinc loss.

A zinc recovery of 95.96 % was achieved when using DRC oxide for neutralisation. The lower soluble zinc loss (when compared to the other scenarios) was attributed to the reduced residue volume and higher wash ratio as a result. SEM images showed this precipitate to be made up of coarse and dense particles, which was supported by the settling rate (of 2.73 and 3.88 m/hr at different polymer dosages) and particle size distribution (with a D_{50} of 16 μm and a D_{90} of 41 μm) of the precipitate. At 2.91 %, the insoluble zinc loss made up the biggest portion of the losses. This outcome was attributed to coating of the zinc-rich neutralising agent with iron precipitate. XRD analyses identified the presence of Plumbo-Jarosite, Gunningite, Anglesite and Magnetite. Since Magnetite is not thermodynamically stable at these experimental conditions, this compound was probably Ferrihydrite.

The addition of a seed recycle to the DRC oxide scenario did not lead to an improvement in the zinc recovery. The recovery decreased to 94.05 %. The increase in the soluble loss from 1.12 to 2.27 % did not appear to be related to particle size or morphology, since the settling rate of the precipitate was very good at 4.92 m/hr and the SEM images showed well defined particles. It was likely due to the higher residue volume as a result of the seed recycle, which negatively impacted the wash ratio. The increase in the insoluble zinc loss (from 2.91 to 3.68 %) was attributed to the 33.33 % reduction in residence time as a result of the 50 % volume seed recycle.

The scenario combining oxide and limestone for neutralisation achieved an excellent zinc recovery of 96.20 %. The low insoluble zinc loss of 0.42 % was attributed to the low average zinc content and increased reactivity of the combination of these neutralising agents compared to calcine. The soluble loss was very high at 3.39 %. While the precipitate appeared to have good settling characteristics with a settling rate of 5.04 m/hr, the SEM images showed that the precipitate was made up of amorphous particles. Therefore, the high soluble zinc loss was due to retention of zinc-rich liquor by the amorphous precipitate and the low wash ratio as a result of the high residue volume.

While the addition of a seed recycle to this scenario gave an excellent zinc recovery of 97.02 %, the settling characteristics of this precipitate was very poor. In fact, the settling test was aborted early. The morphology of the precipitate was not believed to be the cause of the poor settling, since the morphology was not likely to change dramatically with the addition of a seed recycle. Since the addition of a seed recycle increased the residue volume from 250 to 330 cm^3, it was believed that particle crowding contributed to the poor settling.

5.2. PLANT TRIAL:

There was an initial decrease in the soluble loss from approximately 1.4 to 0.8 % with the implementation of a seed recycle at 2 m^3/hr. This was attributed to the presence of seed, which promoted agglomeration growth. The settling rates and particle size distribution of the precipitate appeared to support this notion. The settling rate increased dramatically between the 'no seed' and '2 m^3/hr seed' scenarios. The improvement in settling was attributed to the size and morphology of the precipitate, but also to a decrease in the solution viscosity. The dramatic decrease in solute concentration (which would result in a decrease in solution viscosity) over this same period was likely the biggest reason for the improvement in the settling rates (from around 6 m/hr to 10 m/hr at a 2 m^3/hr seed recycle). There was an increase in the precipitate particle size, especially in the coarse fraction, after the implementation of a seed recycle of 2 m^3/hr.

The soluble zinc loss then increased significantly (to approximately 1.5 %) as the seed recycle rate was increased to 4 and 6 m^3/hr. The reason appeared to be the dramatic increase in the residue volume (from approximately 20 to 40 m^3) and the impact that this had on the belt wash ratio (which decreased from around 1.5 to less than 0.5). The upward trend in the soluble zinc loss was also supported by the settling rates and particle size distribution of the iron residue. The settling rate of the precipitate decreased from a maximum of 10 down to 4 m/hr at the higher seed addition rates. While this was largely attributed to an increase in the solute concentration (and the solution viscosity), the particle size also contributed. The presence of fines was potentially a result of attrition and dis-agglomeration caused by particle crowding, particularly at high seed recycle volumes. While a seed recycle rate of 6 m^3/hr appeared to be excessive, a second increase in the precipitate particle size was evident at this seed addition rate, particularly in the coarse size fraction and in the last two reactors. This finding seemed to support the importance of residence time in agglomeration growth.

The insoluble zinc loss initially increased from approximately 7 % (at no seed addition) to 11 % (at a seed addition rate of 2 m^3/hr). Thereafter, the insoluble zinc loss decreased to an average of 6 % with a further increase in the seed recycle to 4 and 6 m^3/hr. The improvement was attributed to the presence of seed as well as an increase in the operating temperature over this period. The seed provided additional surface area for precipitation and reduced coating of unleached zinc-rich neutralising agent. The SEM images and XRD analyses appeared to support these findings. SEM images showed fewer instances of coating of neutralising agent by iron precipitate in the samples taken at high seed recycle rates. XRD analyses identified Sphalerite (ZnS present in calcine, due to incomplete roasting) and Zincite (the mineral form of zinc oxide) in the residue. The prevalence decreased as the seed recycle rate was increased, until there was almost no Sphalerite or Zincite present in the iron residue samples in the last two weeks of the plant trial. The Magnetite identified in the samples was probably Ferrihydrite, since Magnetite formation was not likely at these plant conditions. Plumbo-Jarosite and Anglesite were also identified. The laboratory work revealed residence time to be an important parameter in minimising the insoluble zinc losses. The residence time decreased during the latter part of the plant trial at the maximum seed addition rates. Any negative impact that this decrease in residence time could have had on the operation was negated by the increase in operating temperature and presence of seed.

Fluoride rejection decreased from approximately 95 % to between 85 and 90 % over the period of the plant trial. An amorphous precipitate adsorbs more impurities than a well-defined crystalline precipitate. The presence of seed promoted the formation of a coarser and denser precipitate, which may have resulted in less adsorption of halides into the precipitate.

In summary, the presence of seed seemed to be beneficial to the Zincor Iron Removal Stage and reduced both the soluble and insoluble zinc losses. A seed recycle of between 2 and 4 m^3/hr (or a 16.67 to 33.33 % volume recycle) appeared to be ideal under these plant conditions.

5.3. SUMMARY:

The tentative conclusions can be summarised as follows:

- The presence of seed reduced the soluble zinc loss by promoting the formation of a coarser and denser precipitate with improved settling and filtration characteristics. Excessive seed addition rates countered the benefits through the negative impact of the high solids loading on the wash

ratio and the potential of particle crowding to hinder settling and cause dis-agglomeration of particles.

- The presence of seed decreased the insoluble zinc loss by making additional surface area available for precipitation, thereby reducing coating of unleached neutralising agent. An excessive seed recycle rate impacted negatively on residence time and countered the potential benefit of seed.
- While the use of limestone as an alternative neutralising agent resulted in a significant decrease in the insoluble portion of the zinc loss, the dramatic increase in the soluble zinc loss eradicated the benefits. The use of limestone for neutralisation generated a large volume of fine and amorphous precipitate with poor settling and filtration characteristics.
- The outcome of this work was sufficiently positive to support a further in-depth study of the use of limestone as an alternative neutralising agent and the implementation of a seed recycle to reduce both the soluble and insoluble zinc losses in the Zincor Iron Removal Stage.

6. RECOMMENDATIONS:

- It is recommended that a thorough plant trial be run over a longer period of time to allow for a detailed economic evaluation and to determine the ideal operating parameters with regards to the seed recycle volume and the HIS iron concentration. A practical and simple procedure for controlling the HIS iron concentration should be developed, since the plant operators appeared to have little understanding of the significance of this parameter and how to control it.
- The main concerns with the use of limestone were that it generated a large amount of fine and amorphous precipitate. These issues could potentially be managed or addressed through an increase in wash ratio, residence time and the implementation of a seed recycle to improve washing efficiency and promote the formation of a coarser and denser precipitate.
- Washing efficiency and solution viscosity were identified as important parameters to minimise the soluble zinc losses. However, an increase in water addition onto the belt filter or into the thickener feed (to reduce viscosity and aid particle settling) was often impossible due to high plant solution inventory. Initiatives that allow for a reduction of water consumption and plant spillages need to be explored. Operator awareness and discipline are also imperative.
- Temperature was identified as a critical parameter, especially with regards to the insoluble zinc losses. The positioning of the heat exchanger resulted in Jarosite scaling, which required regular downtime for cleaning. Circulating slurry from the second reactor, where most of the iron had already been removed, could potentially minimise the scale-up and downtime.
- The use of SEM could be applied more extensively in future studies. Properties such as density and texture of particles, as well as phases formed, can be elaborated on much more to support arguments where other results are less conclusive.

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APPENDIX 1 - PRELIMINARY LABORATORY WORK:

***TABLE 1:** MASS BALANCE – DETERMINING THE EXPERIMENTAL PROCEDURE & EVALUATION OF SEEDING*

	EXPERIMENT 1		EXPERIMENT 2		EXPERIMENT 3		EXPERIMENT 4		EXPERIMENT 5	
IN										
Total volume (litres)	18.00		18.00		18.00		18.00		18.00	
HIS										
Flowrate (ml/min)	38.00		38.00		34.00		50.00		50.00	
Running time (min)	413.00		410.00		405.00		305.00		309.00	
Residence time/reactor (m	68.83		68.33		67.50		50.83		51.50	
Volume (litres)	15.69		15.58		13.77		15.25		15.45	
Solution analysis										
Zn (g/l)	77.30	1213.14 g	75.00	1168.50 g	74.80	1029.00 g	79.30	1209.33 g	80.50	1243.73 g
Fe (g/l)	13.60	213.44 g	16.30	253.95 g	16.20	223.07 g	15.28	233.02 g	15.80	244.11 g
Calcine Slurry										
Volume (litres)	2.31	3168.44 g	2.42	3236.35 g	4.23	5562.45 g	2.75	3638.25 g	2.55	3410.20 g
Slurry SG	1374.00		1337.33		1315.00		1323.00		1337.33	
Solids SG									3.81	
Solution SG	1119.25		1162.00		1110.00		1105.00		1100.00	
Solution analysis (litres)	1.90	2124.97 g	1.87	2170.51 g	3.39	3760.22 g	2.18	2407.79 g	2.09	2299.16 g
Zn (g/l)	24.70	46.89 g	37.90	70.79 g	25.40	86.04 g	25.40	55.35 g	23.30	48.70 g
% solids	32.93		32.93		32.40		33.82		32.58	
Solids analysis		1043.47 g		1065.84 g		1802.23 g		1230.46 g		1111.04 g
Zn (%)	46.88	489.18 g	49.52	527.80 g	48.93	881.83 g	49.71	611.66 g	49.61	551.19 g
Fe (%)	4.84	50.50 g	5.81	61.93 g	5.81	104.71 g	6.12	75.30 g	5.93	65.88 g
OUT										
Total volume (litres)	18.00	24786.00 g	18.00	24391.80 g	18.00	24865.20 g	18.00	24714.00 g	18.00	24192.00 g
Slurry SG	1377.00		1355.10		1381.40		1373.00		1344.00	
Solids SG	3099.00		3903.00		3363.00		3179.00		2896.00	
Solution SG	1318.19		1318.19		1318.19		1342.67		1312.16	
% solids	7.43		4.11		7.53		3.82		4.33	
Solids analysis (g)		1842.25 g		1003.27 g		1871.33 g		945.22 g		1047.98 g
Wet mass							62.02		30.00	
Dry mass							29.47		12.84	
Zn (%)	10.66	196.38 g	15.31	153.60 g	8.94	108.80 g	13.76	130.06 g	10.50	127.78
Fe (%)	37.06	682.74 g	28.52	286.13 g	34.93	425.09 g	30.47	370.81 g	33.29	405.13 g
H_2O (%)	55.43	2291.13 g	54.50	1201.89 g	54.50	2241.79 g	52.48	1043.88 g	57.19	1400.00 g
Solution analysis (litres)	17.41	22943.75 g	17.74	23388.53 g	17.44	22993.87 g	17.70	23768.78 g	17.64	23144.02 g
Zn (g/l)	108.90	1895.46 g	115.00	2040.44 g	120.00	2093.23 g	112.30	1988.01 g	106.50	1878.46 g
Fe (ppm)	3.70	0.06 g	5.60	0.10 g	3.10	71.28 g	10.70	2.54 g	17.00	3.93 g
Wash (litres)	0.50	489.60 g	0.50	489.60 g	0.50	489.60 g	0.50	491.73 g	0.50	484.36 g
Washing efficiency (%)	75.00		75.00		75.00		75.00		75.00	
Solution SG	1021.24		1021.24		1021.24		1016.82		1032.29	
Zn (g/l)	18.40	9.20 g	6.90	3.45 g	11.00	5.50 g	7.00	3.50 g	12.90	0.48 g
Fe (ppm)	1.50	0.00075 g	1.80	0.0009 g	1.80	0.0009 g	1.80	0.0009 g	1.80	0.0009 g

***TABLE 2:* MASS BALANCE – IDENTIFYING ALTERNATIVE NEUTRALISING AGENTS**

	OXIDES		ETP U/F		BZS		LIME		LIMESTONE		BH & BA	
IN												
SEED												
Volume (litres)	2.50	3360.00 g	2.50	3360.00 g	2.50	3360.00 g	2.50	3360.00 g	2.50	3360.00 g	2.50	3360.00 g
Solution analysis (litr	2.45	3214.45 g	2.45	3214.45 g	2.45	3214.45 g	2.45	3214.45 g	2.45	3214.45 g	2.45	3214.45 g
Filtrate SG	1312.16		1312.16		1312.16		1312.16		1312.16		1312.16	
Zn (g/l)	106.50	260.90 g	106.50	260.90 g	106.50	260.90 g	106.50	260.90 g	106.50	260.90 g	106.50	260.90 g
Fe (ppm)	17.00	41.65 g	17.00	41.65 g	17.00	41.65 g	17.00	41.65 g	17.00	41.65 g	17.00	41.65 g
Solids analysis		145.55 g		145.55 g		145.55 g		145.55 g		145.55 g		145.55 g
Wet mass (g)	57.17		57.17		57.17		57.17		57.17		57.17	
Dry mass (g)	24.47		24.47		24.47		24.47		24.47		24.47	
Slurry SG	1344.00		1344.00		1344.00		1344.00		1344.00		1344.00	
Solids SG	2896.00		2896.00		2896.00		2896.00		2896.00		2896.00	
% Solids	4.33		4.33		4.33		4.33		4.33		4.33	
Zn (%)	10.50	15.28 g	10.50	15.28 g	10.50	15.28 g	10.50	15.28 g	10.50	15.28 g	10.50	15.28 g
Fe (%)	33.29	48.45 g	33.29	48.45 g	33.29	48.45 g	33.29	48.45 g	33.29	48.45 g	33.29	48.45 g
H_2O (%)	57.19	194.44 g	57.19	194.44 g	57.19	194.44 g	57.19	194.44 g	57.19	194.44 g	57.19	194.44 g
HIS												
Running time (min)	85.00		70.50		85.00		72.00		72.00		69.00	
Flowrate (ml/min)	42.00		15.74		30.00		50.00		43.00		55.00	
Volume (litres)	3.57		1.11		2.55		3.60		3.10		3.80	
Solution analysis												
Zn (g/l)	75.50	269.54 g	74.00	82.10 g	76.80	195.84 g	74.00	266.40 g	69.50	215.17 g	66.40	251.99 g
Fe (g/l)	14.10	50.34 g	14.20	15.75 g	14.50	36.98 g	14.80	53.28 g	13.90	43.03 g	12.30	46.68 g
H_2SO_4 (g/l)	7.80	27.85 g	7.00	7.77 g	7.40	18.87 g	7.00	25.20 g	6.80	21.05 g	6.60	25.05 g
F (g/l)	0.00	0.011 g	0.00	0.01 g	0.00	0.01 g	0.00	0.01 g	0.00	0.01 g	0.00	0.01 g
Cl (g/l)											0.40	1.43 g
Ca (g/l)			259.00	0.29 g	272.00	0.69 g	272.00	0.98 g				
Mn (g/l)			11.10	12.32 g	10.37	26.44 g						
Mg (g/l)			7.82	8.68 g	7.57	19.30 g						
NEUTRALISING AGENT:												
Volume (litres)	0.43	517.72 g	2.89	3026.35 g	1.45	1761.75 g	0.40	431.60 g	0.90	988.07 g	0.21	254.00 g
Slurry SG	1204.00		1047.00		1215.00		1079.00		1093.00		1239.00	
Carrier liquid SG	1000.00		1005.00		1000.00		1000.00		1000.00		1000.00	
% Solids	28.00		24.78		27.60		19.52		9.23		25.69	
Solids density	6000.00		2885.00		3120.00		2280.00		2665.00		6000.00	
Solids analysis		144.96 g		749.93 g		486.24 g		84.25 g		91.20 g		65.25 g
Zn (%)	70.11	101.63 g	12.70	95.24 g	12.79	62.19 g					83.45	54.45 g
Fe (%)	0.78	1.13 g	1.53	11.47 g	0.13	0.63 g					0.11	0.07 g
Ca (%)	0.18	0.26 g	16.21	121.56 g	19.68	95.69 g	49.57	41.76 g	37.52	34.22 g		
SiO_2 (%)							1.00	0.84 g	0.72	0.66 g		
F (%)	0.04	0.05 g									0.00	0.00 g
Mn (%)			2.50	18.75 g	0.62	3.01 g						
Mg (%)			2.42	18.15 g	0.09	0.44 g						
Solution	0.37	372.76 g	2.29	2276.42 g	1.28	1275.51 g	0.35	347.35 g	0.90	896.87 g	0.19	188.74 g
OUT												
Fe SLURRY												
Volume (litres)	4.00	5240.00 g	4.00	4840.00 g	4.00	5223.20 g	4.00	5155.20 g	4.00	5033.20 g	4.00	5160.00 g
Slurry SG	1310.00		1210.00		1305.80		1288.80		1258.30		1290.00	
Solution SG	1285.87		1167.33		1269.81		1238.83		1225.17		1256.42	
% Solids	3.65		5.83		5.50		6.87		4.57		4.54	
Solids density	2599.00		2956.00		2547.00		2845.00		2894.00		2949.00	
Solids analysis		191.01 g		282.05 g		287.06 g		354.04 g		229.82 g		234.04 g
Zn (%)	5.38	10.28 g	3.03	8.55 g	1.42	4.08 g	2.91	10.30 g	1.67	3.84 g	8.90	20.83 g
Fe (%)	33.08	63.19 g	20.64	58.21 g	9.59	27.53 g	20.30	71.87 g	22.78	52.35 g	34.58	80.93 g
Ca (%)	0.41	0.78 g	10.37	29.25 g	18.57	53.31 g	0.41	1.45 g	0.41	0.94 g	0.41	0.96 g
SiO_2 (%)							1.15	4.07 g	1.24	2.85 g		
F (%)	0.02	0.03 g									0.01	0.02 g
H_2O (%)	54.00	224.23 g	57.59	383.00 g	51.57	305.67 g	57.59	480.76 g	61.27	363.57 g	54.89	284.78 g
Mn (%)			1.39	3.92 g	0.37	1.06 g						
Mg (%)			0.06	0.17 g	0.08	0.23 g						
Cl (%)											0.01	0.02 g
Solution analysis (litr	3.93	5048.99 g	3.90	4557.95 g	3.89	4936.14 g	3.88	4801.16 g	3.92	4803.38 g	3.92	4925.96 g
Zn (g/l)	91.50	359.28 g	53.50	208.90 g	84.00	326.53 g	76.00	294.54 g	70.50	276.40 g	90.50	354.82 g
Fe (ppm)	255.00	1.00 g	87.00	0.34 g	74.00	0.29 g	117.00	0.45 g	128.00	0.50 g	950.00	3.72 g
SO_4 (%)					182.00	707.49 g						
Ca (g/l)			598.00	2.33 g	538.00	2.09 g	564.00	2.19 g	572.00	2.24 g		
SiO_2 (g/l)							113.00	0.44 g	130.00	0.51 g		
F (g/l)	0.001										0.04	0.00 g
Mn (g/l)			6.60	25.77 g	9.84	38.25 g						
Mg (g/l)			5.47	21.36 g	7.13	27.72 g						
Cl (ppm)											456.00	1.79 g
Wash (litres)	0.25		0.25		0.25		0.25		0.25		0.25	
Efficiency (%)	75.00		75.00		75.00		75.00		75.00		75.00	
Solution SG	1033.16		1018.15		1066.17		1085.93		1055.53		1023.52	
Zn (g/l)	25.90	6.48 g	9.90	2.48 g	24.10	6.03 g	11.10	2.78 g	18.00	4.50 g	8.80	2.20 g

APPENDIX 2 – FINAL LABORATORY WORK:

***TABLE 3:** MASS BALANCE – EVALUATING ALTERNATIVE NEUTRALISING AGENTS AND A SEED RECYCLE*

	LIMESTONE		DRC OXIDE		DRC OXIDE (SEED)		DRC OXIDE/LIMESTONE		DRC OXIDE/LIMESTONE (SEED)	
IN:										
Total volume (litres)	12.00		12.00		12.00		12.00		12.00	
HIS										
Flowrate (ml/min)	44.07		37.06		41.72		42.96		39.50	
Running time (min)	214.00		255.00		160.60		235.00		160.00	
Volume (litres)	9.43		9.45		6.70		10.10		6.32	
Solution analysis										
Zn (g/l)	69.10	651.75 g	69.10	652.00 g	69.10	462.98 g	69.10	697.67 g	69.10	436.71 g
Fe (g/l)	14.70	138.65 g	14.70	138.92 g	14.70	98.49 g	14.70	148.42 g	14.70	92.90 g
Fe(II) (g/l)	0.53	4.95 g	0.53	4.96 g	0.53	3.52 g	0.53	5.30 g	0.53	3.32 g
H_2SO_4 (g/l)	6.95	65.55 g	6.95	65.68 g	6.95	46.57 g	6.95	70.17 g	6.95	43.92 g
ACID WASH (HIS)										
Flowrate (ml/min)	2.00		1.00		2.00		1.50		1.50	
Running time (min)	214.00		255.00		160.60		235.00		160.00	
Volume (litres)	0.43		0.26		0.32		0.35		0.24	
SEED										
Volume (litres)	2.50	3766.00 g	2.50	3305.00 g	4.02	5222.85 g	2.00	2628.80 g	4.00	5206.00 g
Slurry SG	1506.40		1322.00		1300.83		1314.40		1301.50	
Solids SG	3177.00		2969.00		3061.00		3075.00		3067.00	
Solution SG	1251.16		1285.78		1270.00		1268.23		1266.08	
Solution analysis	2.17	2713.35 g	2.45	3145.28 g	3.95	5011.27 g	1.95	2471.66 g	3.92	4964.72 g
Zn (g/l)	71.40	154.84 g	86.30	211.11 g	89.40	352.76 g	87.80	171.11 g	89.80	352.14 g
% solids	27.95		4.83		4.05		5.98		4.63	
Fe (g/l)	0.50	1.08 g	0.50	1.22 g	0.90	3.55 g	0.86	1.68 g	0.93	3.65 g
Solids analysis		1052.65 g		159.72 g		211.58 g		157.14 g		241.28 g
Zn (%)	0.16	1.68 g	0.86	1.37 g	6.95	14.70 g	5.74	9.02 g	5.57	13.44 g
Fe (%)	20.55	216.32 g	37.81	60.39 g	26.80	56.70 g	29.87	46.94 g	28.45	68.65 g
LIMESTONE										
Volume (litres)	2.14	2394.66 g					0.71	788.90 g	0.48	537.12 g
Slurry SG	1119.00						1119.00		1119.00	
Solids SG	2707.00						2707.00		2707.00	
Solution SG	1000.00						1000.00		1000.00	
Solution analysis		1936.56 g					0.64	637.98 g	0.43	434.37 g
% solids	19.13						19.13		19.13	
Solids analysis		458.10 g						150.92 g		102.75 g
Zn (%)	0.19	0.87 g					0.19	0.29 g	0.19	0.20 g
Fe (%)	0.17	0.78 g					0.17	0.26 g	0.17	0.17 g
Ca (%)	38.41	175.96 g					38.41	57.97 g	38.41	39.47 g
DRC OXIDE										
Volume (litres)			2.30	2666.79 g	0.96	1119.70 g	0.85	983.05 g	0.96	1115.52 g
Slurry SG			1162.00		1162.00		1162.00		1162.00	
Solids SG			6309.00		6309.00		6309.00		6309.00	
Solution SG			1000.00		1000.00		1000.00		1000.00	
Solution analysis				2202.77 g		924.87 g		812.00 g		921.42 g
% solids			17.40		17.40		17.40		17.40	
Solids analysis				464.02 g		194.83 g		171.05 g		194.10 g
Zn (%)			68.82	319.34 g	68.82	134.08 g	68.82	117.72 g	68.82	133.58 g
Fe (%)			0.78	3.62 g	0.78	1.52 g	0.78	1.33 g	0.78	1.52 g
Ca (%)			0.15	0.70 g	0.15	0.29 g	0.15	0.26 g	0.15	0.29 g
OUT										
Total volume (litres)	12.00	15347.20 g	12.00	15537.00 g	12.00	15618.00 g	12.00	15664.80 g	12.00	15772.80 g
Slurry SG	1278.93		1294.75		1301.50		1305.40		1314.40	
Solids SG	3282.00		3288.00		3067.00		3127.00		3060.00	
Solution SG	1216.22		1266.92		1266.08		1266.66		1265.00	
% solids	7.79		3.50		4.63		4.99		6.41	
Solids analysis		1195.70 g		543.30 g		723.85 g		781.41 g		1010.57 g
Wet mass (g)	74.33		88.01				108.08		69.53	
Dry mass (g)	36.63		44.54				60.99		44.78	
Cake thickness (mm)	14.00		11.15		13.25		18.00		11.50	
Area (cm^2)	50.00		50.00		50.00		50.00		50.00	
Zn (%)	0.80	9.57 g	5.74	31.19 g	5.57	40.32 g	0.53	4.14 g	0.54	5.46 g
Fe (%)	18.18	217.38 g	29.87	162.28 g	28.45	205.94 g	28.44	222.23 g	27.06	273.46 g
Ca (%)	15.09	180.43 g	0.09	0.49 g	0.08	0.58 g	7.48	58.45 g	8.27	83.57 g
H_2O (%)	50.72	1230.64 g	49.39	530.21 g	54.75	875.82 g	56.43	1012.04 g	64.41	1828.90 g
Solution analysis	11.64		11.83		11.76		11.75		11.67	
Zn (g/l)	65.30	759.81 g	87.80	1039.09 g	89.80	1056.41 g	83.90	985.83 g	89.50	1044.44 g
Fe (g/l)	0.34	3.96 g	0.48	5.68 g	0.54	6.35 g	0.46	5.41 g	0.38	4.43 g
Fe(II) (g/l)	0.21	2.44 g	0.38	4.50 g	0.39	4.59 g	0.34	4.00 g	0.28	3.27 g
Ca (g/l)	0.47	5.48 g	0.32	3.82 g	0.35	4.12 g	0.44	5.15 g	0.47	5.52 g

APPENDIX 3 – PLANT TRIAL:

***TABLE 4:** MASS BALANCE – EVALUATING DRC OXIDE TOGETHER WITH A SEED RECYCLE (PART 1)*

IN	9-Oct-11		11-Oct-11		12-Oct-11		13-Oct-11		14-Oct-11		15-Oct-11		17-Oct-11		18-Oct-11		19-Oct-11	
Total volume (m³)	1336.00		1561.00		1530.00		1268.00		1459.00		1502.00		1564.00		1827.00		1540.00	
Running time (hrs)	24.00		24.00		24.00		24.00		24.00		24.00		24.00		24.00		24.00	
Flowrate (m³/hr)	55.67		65.04		63.75		52.83		60.79		62.58		65.17		76.13		64.17	
HIS																		
Flowrate (m³/hr)	44.29		48.92		48.88		39.25		45.29		46.42		47.32		55.04		47.00	
Volume (m³)	1063.00		1174.00		1173.00		942.00		1087.00		1114.00		1150.00		1321.00		1128.00	
Solution analysis																		
Zn (g/l)	43.00	44.33 t	69.50	71.65 t	69.30	71.45 t	73.00	75.26 t	77.50	79.90 t	77.80	80.21 t	72.00	74.23 t	74.50	76.81 t	73.50	75.78 t
Fe(II) (g/l)	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t	0.87	0.90 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t
Fe(III) (g/l)	6.93	7.14 t	11.25	11.60 t	12.56	12.95 t	11.67	12.03 t	15.14	15.61 t	16.57	17.08 t	14.47	14.92 t	13.72	14.15 t	12.90	13.30 t
F (g/l)	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
H_2SO_4 (g/l)	21.20	21.86 t	25.20	25.98 t	22.00	22.68 t	20.60	21.24 t	16.60	17.11 t	20.40	21.03 t	26.20	27.01 t	32.00	32.99 t	26.40	27.22 t
ACID WASH (HIS)																		
Flowrate (m³/hr)	2.46		4.50		3.71		3.63		3.96		3.25		2.92		3.50		2.21	
Volume (m³)	59.00		108.00		89.00		87.00		95.00		78.00		70.00		84.00		53.00	
SEED																		
Flowrate (m³/hr)	1.92		3.83		3.83		3.83		3.83		3.83		5.75		5.75		5.75	
Volume (m³)	46.00		92.00		92.00		92.00		92.00		92.00		138.00		138.00		138.00	
CALCINE																		
Flowrate (m³/hr)	4.00		4.25		4.04		4.08		4.04		4.04		3.83		6.29		4.54	
Volume (m³)	96.00	151.04 t	102.00	165.24 t	97.00	153.02 t	98.00	152.39 t	97.00	155.20 t	97.00	157.14 t	92.00	149.04 t	151.00	235.56 t	109.00	167.86 t
Slurry SG	1573.33		1620.00		1577.50		1555.00		1600.00		1620.00		1620.00		1560.00		1540.00	
Solids SG	5082.00		5364.00		5621.00		5558.00		5722.00		5709.00		5346.00		5897.00		5901.00	
Solution SG	1230.00		1258.00		1266.00		1266.00		1266.00		1274.00		1272.00		1261.00		1256.00	
% solids	28.79		29.19		25.49		24.07		26.81		27.49		28.19		24.36		23.43	
Solution analysis	67.44	107.56 t	93.01	117.00 t	90.06	114.02 t	91.40	115.71 t	89.73	113.60 t	89.43	113.94 t	84.14	107.03 t	141.26	179.13 t	102.34	128.53 t
Zn (g/l)	70.00	5.77 t	81.50	6.71 t	80.50	6.63 t	80.50	6.63 t	90.00	7.41 t	93.30	7.69 t	91.00	7.50 t	94.00	7.74 t	87.50	7.21 t
Fe(II) (g/l)	0.03	0.00 t	0.04	0.00 t	0.06	0.00 t	0.27	0.02 t	0.22	0.02 t	0.13	0.01 t	0.12	0.01 t	0.19	0.02 t	0.13	0.01 t
Fe(III) (g/l)	0.15	0.01 t	0.18	0.01 t	6.59	0.54 t	4.92	0.41 t	0.20	0.02 t	0.21	0.02 t	0.29	0.02 t	0.15	0.01 t	0.15	0.01 t
F (g/l)	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
Solids analysis		43.48 t		48.24 t		39.00 t		36.68 t		41.60 t		43.20 t		42.01 t		57.43 t		39.33 t
Zn (%)	58.44	21.04 t	56.79	20.45 t	58.96	21.23 t	56.51	20.35 t	56.70	20.42 t	56.76	20.44 t	59.05	21.26 t	57.79	20.81 t	59.72	21.51 t
Fe (%)	4.98	1.79 t	5.20	1.87 t	5.50	1.98 t	5.49	1.98 t	5.35	1.93 t	5.37	1.93 t	5.41	1.95 t	5.39	1.94 t	5.47	1.97 t
OXIDES																		
Flowrate (m³/hr)	3.00		3.54		3.29		2.04		3.67		5.04		4.75		5.54		4.67	
Volume (m³)	72.00	93.60 t	85.00	110.50 t	79.00	102.70 t	49.00	63.70 t	88.00	114.40 t	121.00	157.30 t	114.00	148.20 t	133.00	172.90 t	112.00	145.60 t
Slurry SG	1300.00		1300.00		1300.00		1300.00		1300.00		1300.00		1300.00		1300.00		1300.00	
Solids SG	5623.00		5688.00		5888.00		5888.00		5888.00		5888.00		5126.00		5126.00		5126.00	
Solution SG	1000.00		1000.00		1000.00		1000.00		1000.00		1000.00		1000.00		1000.00		1000.00	
% solids	28.07		27.80		27.80		27.80		27.80		27.80		28.67		28.67		28.67	
Solution analysis	67.33	67.33 t	79.78	79.78 t	74.15	74.15 t	45.99	45.99 t	82.60	82.60 t	113.57	113.57 t	105.71	105.71 t	123.33	123.33 t	103.86	103.86 t
Solids analysis		26.27 t		30.72 t		28.55 t		17.71 t		31.80 t		43.73 t		42.49 t		49.57 t		41.74 t
Zn (%)	66.93	27.75 t	66.84	27.71 t	66.84	27.71 t	66.84	27.71 t	66.84	27.71 t	66.84	27.71 t	69.48	28.81 t	69.48	28.81 t	69.48	28.81 t
Fe (%)	1.24	0.51 t	1.30	0.54 t	1.30	0.54 t	1.30	0.54 t	1.30	0.54 t	1.30	0.54 t	1.16	0.48 t	1.16	0.48 t	1.16	0.48 t
F (%)	0.03	0.01 t	0.03	0.013 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t
OUT	**9-Oct-11**		**11-Oct-11**		**12-Oct-11**		**13-Oct-11**		**14-Oct-11**		**15-Oct-11**		**17-Oct-11**		**18-Oct-11**		**19-Oct-11**	
Total volume (m³)	1336.00		1561.00		1530.00		1268.00		1459.00		1502.00		1564.00		1827.00		1540.00	
Running time (hrs)	24.00		24.00		24.00		24.00		24.00		24.00		24.00		24.00		24.00	
THICKENER O/F																		
Flowrate (m³/hr)	42.50		50.38		50.42		44.17		42.04		51.08		46.67		55.67		50.38	
Volume (m³)	1020.00		1209.00		1210.00		1060.00		1009.00		1226.00		1120.00		1336.00		1209.00	
Solution SG	1230.00		1258.00		1266.00		1266.00		1266.00		1274.00		1272.00		1261.00		1256.00	
Solution analysis																		
Zn (g/l)	70.00	71.47 t	81.50	83.21 t	80.50	82.19 t	80.50	82.19 t	90.00	91.89 t	93.30	95.26 t	91.00	92.91 t	94.00	95.97 t	87.50	89.34 t
Fe(II) (g/l)	0.03	0.03 t	0.04	0.04 t	0.06	0.06 t	0.27	0.28 t	0.22	0.22 t	0.13	0.13 t	0.12	0.12 t	0.19	0.19 t	0.13	0.13 t
Fe(III) (g/l)	0.15	0.15 t	0.18	0.18 t	6.59	6.73 t	4.92	5.02 t	0.20	0.20 t	0.21	0.21 t	0.29	0.30 t	0.15	0.15 t	0.15	0.15 t
F (g/l)	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
THICKENER U/F																		
Flowrate (m³/hr)	11.79		11.42		11.46		11.50		11.38		11.79		11.75		10.96		11.04	
Volume (m³)	283.00	385.68 t	274.00	400.41 t	275.00	407.33 t	276.00	408.76 t	273.00	404.60 t	283.00	420.73 t	282.00	435.02 t	263.00	404.09 t	265.00	401.83 t
Slurry SG	1362.82		1461.33		1461.18		1461.00		1462.80		1466.67		1542.64		1536.45		1536.33	
Solids SG	3387.00		3752.00		3202.00		3203.00		3134.00		3136.00		3270.00		3224.00		3763.00	
Solution SG	1230.00		1258.00		1266.00		1266.00		1266.00		1274.00		1272.00		1261.00		1256.00	
% solids	15.28		23.16		24.03		24.01		24.53		24.09		28.71		29.44		28.46	
Solids analysis		58.92 t		92.72 t		97.87 t		98.12 t		99.30 t		101.36 t		124.91 t		118.98 t		114.43 t
Sol Zn (%)	0.60		0.37		1.44		3.52		2.60		2.60		3.23		0.72		2.93	
Zn (%)	10.05	8.62 t	9.99	8.57 t	10.04	8.61 t	10.04	8.61 t	7.86	6.74 t	8.25	7.07 t	7.22	6.19 t	6.72	5.76 t	9.55	8.19 t
Fe (%)	26.66	22.86 t	28.61	24.53 t	29.44	25.24 t	28.02	24.02 t	30.07	25.78 t	28.61	24.53 t	31.48	26.99 t	32.25	27.65 t	28.85	24.73 t
F (%)	0.02	0.01 t	0.02	0.014 t	0.02	0.01 t	0.02	0.01 t	0.02	0.014 t	0.02	0.01 t	0.02	0.021 t	0.02	0.02 t	0.02	0.021 t
Solution analysis	265.65	326.76 t	244.58	307.69 t	244.43	309.45 t	245.36	310.63 t	241.32	305.51 t	250.68	315.36 t	243.80	310.12 t	226.09	285.10 t	229.82	287.40 t
Zn (g/l)	70.00	16.60 t	81.50	19.33 t	80.50	19.10 t	80.50	19.10 t	90.00	21.35 t	93.30	22.13 t	91.00	21.59 t	94.00	22.30 t	87.50	20.76 t
Fe(II) (g/l)	0.03	0.01 t	0.04	0.01 t	0.06	0.01 t	0.27	0.06 t	0.22	0.05 t	0.13	0.03 t	0.12	0.03 t	0.19	0.05 t	0.13	0.03 t
Fe(III) (g/l)	0.15	0.04 t	0.18	0.04 t	6.59	1.56 t	4.92	1.17 t	0.20	0.05 t	0.21	0.05 t	0.29	0.07 t	0.15	0.04 t	0.15	0.04 t
F (g/l)	0.00	0.00 t		0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
Fe CAKE																		
Moisture	53.26	67.14 t	49.44	90.66 t	49.78	97.01 t	48.88	93.82 t	47.62	90.28 t	45.11	83.30 t	47.89	114.79 t	49.52	116.72 t	49.02	110.03

TABLE 5: MASS BALANCE – EVALUATING DRC OXIDE TOGETHER WITH A SEED RECYCLE (PART 2)

IN	27-Sep-11		30-Sep-11		1-Oct-11		2-Oct-11		5-Oct-11		6-Oct-11		7-Oct-11		8-Oct-11	
Total volume (m^3)	1285.00		1481.00		1464.00		1438.00		1588.00		1594.00		1278.00		1458.00	
Running time (hrs)	24.00		24.00		24.00		24.00		24.00		24.00		24.00		24.00	
Flowrate (m^3/hr)	53.54		61.71		61.00		59.92		66.17		66.42		53.25		60.75	
HIS																
Flowrate (m^3/hr)	42.96		47.25		47.25		46.83		52.83		54.00		43.46		50.08	
Volume (m^3)	1031.00		1134.00		1134.00		1124.00		1268.00		1296.00		1043.00		1202.00	
Solution analysis																
Zn (g/l)	70.00	72.17 t	70.00	72.17 t	69.80	71.96 t	62.80	64.75 t	57.30	59.08 t	60.50	62.38 t	46.00	47.43 t	47.30	48.77 t
Fe(II) (g/l)	0.22	0.23 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t	0.01	0.01 t
Fe(III) (g/l)	14.12	14.56 t	12.51	12.90 t	10.99	11.33 t	9.66	9.96 t	5.33	5.50 t	5.43	5.60 t	6.76	6.97 t	5.53	5.70 t
F (g/l)	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
H_2SO_4 (g/l)	20.20	20.83 t	23.90	24.64 t	26.20	27.01 t	26.80	27.63 t	33.20	34.23 t	34.10	35.16 t	20.10	20.72 t	23.50	24.23 t
ACID WASH (HIS)																
Flowrate (m^3/hr)	2.13		4.58		5.21		4.83		3.42		3.13		2.42		2.46	
Volume (m^3)	51.00		110.00		125.00		116.00		82.00		75.00		58.00		59.00	
SEED																
Flowrate (m^3/hr)	0.00		0.00		0.00		0.00		1.92		1.92		1.92		1.92	
Volume (m^3)	0.00		0.00		0.00		0.00		46.00		46.00		46.00		46.00	
CALCINE																
Flowrate (m^3/hr)	3.71		5.50		4.96		4.08		4.00		4.13		3.42		4.00	
Volume (m^3)	89.00	138.98 t	132.00	211.20 t	119.00	192.78 t	98.00	158.76 t	96.00	155.20 t	99.00	158.40 t	82.00	127.92 t	96.00	152.96 t
Slurry SG	1561.63		1600.00		1620.00		1620.00		1616.67		1600.00		1560.00		1593.33	
Solids SG	5439.00		5183.00		5075.00		5338.00		5162.00		5957.00		5300.00		5563.00	
Solution SG	1250.00		1248.00		1252.00		1246.00		1230.00		1234.00		1226.00		1224.00	
% solids	25.91		28.98		30.16		30.12		31.40		28.85		27.85		29.72	
Solution analysis	82.38	102.97 t	120.19	150.00 t	107.55	134.65 t	89.04	110.95 t	86.56	106.47 t	91.33	112.70 t	75.28	92.29 t	87.83	107.50 t
Zn (g/l)	87.50	7.21 t	83.50	6.88 t	83.80	6.90 t	84.00	6.92 t	74.00	6.10 t	76.00	6.26 t	74.00	6.10 t	71.00	5.85 t
Fe(II) (g/l)	0.03	0.00 t	0.03	0.00 t	0.01	0.00 t	0.04	0.00 t	0.04	0.00 t	0.03	0.00 t	0.04	0.00 t	0.04	0.00 t
Fe(III) (g/l)	0.12	0.01 t	0.24	0.02 t	0.18	0.01 t	0.06	0.00 t	0.14	0.01 t	0.15	0.01 t	0.08	0.01 t	0.15	0.01 t
F (g/l)	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
Solids analysis		36.01 t		61.20 t		58.13 t		47.81 t		48.73 t		45.70 t		35.63 t		45.46 t
Zn (%)	60.62	21.83 t	58.18	20.95 t	57.90	20.85 t	59.36	21.38 t	59.74	21.51 t	58.31	21.00 t	57.05	20.54 t	56.90	20.49 t
Fe (%)	5.43	1.96 t	6.20	2.23 t	5.94	2.14 t	6.02	2.17 t	5.33	1.92 t	5.24	1.89 t	5.32	1.92 t	4.95	1.78 t
OXIDES																
Flowrate (m^3/hr)	4.75		4.38		3.58		4.17		4.00		3.25		2.04		2.29	
Volume (m^3)	114.00	148.20 t	105.00	136.50 t	86.00	111.80 t	100.00	130.00 t	96.00	124.80 t	78.00	101.40 t	49.00	63.70 t	55.00	71.50 t
Slurry SG	1300.00		1300.00		1300.00		1300.00		1300.00		1300.00		1300.00		1300.00	
Solids SG	5708.00		4600.00		5676.00		5239.00		5623.00		5623.00		5623.00		5623.00	
Solution SG	1000.00		1000.00		1000.00		1000.00		1000.00		1000.00		1000.00		1000.00	
% solids	27.98		29.49		28.01		28.52		28.07		28.07		28.07		28.07	
Solution analysis	106.74	106.74 t	96.25	96.25 t	80.48	80.48 t	92.92	92.92 t	89.77	89.77 t	72.94	72.94 t	45.82	45.82 t	51.43	51.43 t
Solids analysis		41.46 t		40.25 t		31.32 t		37.08 t		35.03 t		28.46 t		17.88 t		20.07 t
Zn (%)	70.30	29.15 t	67.87	28.14 t	65.30	27.08 t	63.56	26.35 t	66.93	27.75 t	66.93	27.75 t	66.93	27.75 t	66.93	27.75 t
Fe (%)	1.02	0.42 t	0.75	0.31 t	0.85	0.35 t	0.99	0.41 t	1.24	0.51 t	1.24	0.51 t	1.24	0.51 t	1.24	0.51 t
F (%)	0.04	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t	0.03	0.01 t
OUT	**27-Sep-11**		**30-Sep-11**		**1-Oct-11**		**2-Oct-11**		**5-Oct-11**		**6-Oct-11**		**7-Oct-11**		**8-Oct-11**	
Total volume (m^3)	1285.00		1481.00		1464.00		1438.00		1588.00		1594.00		1278.00		1458.00	
Running time (hrs)	24.00		24.00		24.00		24.00		24.00		24.00		24.00		24.00	
THICKENER O/F																
Flowrate (m^3/hr)	42.54		53.25		51.79		55.63		56.63		55.08		50.25		53.42	
Volume (m^3)	1021.00		1278.00		1243.00		1335.00		1359.00		1322.00		1206.00		1282.00	
Solution SG	1250.00		1248.00		1252.00		1246.00		1230.00		1234.00		1226.00		1224.00	
Solution analysis																
Zn (g/l)	87.50	89.34 t	83.50	85.25 t	83.80	85.56 t	84.00	85.76 t	74.00	75.55 t	76.00	77.60 t	74.00	75.55 t	71.00	72.49 t
Fe(II) (g/l)	0.03	0.03 t	0.03	0.03 t	0.01	0.01 t	0.04	0.04 t	0.04	0.04 t	0.03	0.03 t	0.04	0.04 t	0.04	0.04 t
Fe(III) (g/l)	0.12	0.12 t	0.24	0.25 t	0.18	0.18 t	0.06	0.06 t	0.14	0.14 t	0.15	0.15 t	0.08	0.08 t	0.15	0.15 t
F (g/l)	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
THICKENER U/F																
Flowrate (m^3/hr)	11.00		11.17		13.54		13.25		11.46		11.29		9.71		11.54	
Volume (m^3)	264.00	382.25 t	268.00	382.84 t	325.00	457.63 t	318.00	435.02 t	275.00	374.13 t	271.00	367.14 t	233.00	314.76 t	277.00	375.43 t
Slurry SG	1447.90		1428.50		1408.09		1368.00		1360.45		1354.75		1350.90		1355.33	
Solids SG	3200.00		3188.00		3150.00		3210.00		3161.00		3484.00		3224.00		3515.00	
Solution SG	1250.00		1248.00		1252.00		1246.00		1230.00		1234.00		1226.00		1224.00	
% solids	22.43		20.76		18.40		14.58		15.70		13.80		14.92		14.87	
Solids analysis		85.74 t		79.49 t		84.19 t		63.41 t		58.73 t		50.67 t		46.96 t		55.82 t
Sol Zn (%)	2.89		0.30		0.30		0.26		0.46		1.35		1.00		1.00	
Zn (%)	9.78	8.39 t	9.28	7.96 t	11.48	9.84 t	11.02	9.45 t	12.04	10.32 t	11.89	10.19 t	11.39	9.77 t	9.38	8.04 t
Fe (%)	33.53	28.75 t	31.43	26.95 t	29.04	24.90 t	29.99	25.71 t	26.99	23.14 t	25.64	21.98 t	26.85	23.02 t	26.18	22.45 t
F (%)	0.02	0.02 t	0.02	0.02 t	0.02	0.01 t	0.02	0.02 t	0.02	0.02 t	0.02	0.02 t	0.02	0.02 t	0.02	0.01 t
Solution analysis	237.21	296.51 t	243.06	303.35 t	298.27	373.44 t	298.25	371.62 t	256.42	315.40 t	256.46	316.47 t	218.43	267.80 t	261.12	319.61 t
Zn (g/l)	87.50	20.76 t	83.50	19.81 t	83.80	19.88 t	84.00	19.93 t	74.00	17.55 t	76.00	18.03 t	74.00	17.55 t	71.00	16.84 t
Fe(II) (g/l)	0.03	0.01 t	0.03	0.01 t	0.01	0.00 t	0.04	0.01 t	0.04	0.01 t	0.03	0.01 t	0.04	0.01 t	0.04	0.01 t
Fe(III) (g/l)	0.12	0.03 t	0.24	0.06 t	0.18	0.04 t	0.06	0.01 t	0.14	0.03 t	0.15	0.04 t	0.08	0.01	0.15	0.03 t
F (g/l)	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t	0.00	0.00 t
Fe CAKE																
Moisture	56.05	109.34 t	56.32	102.50 t	51.38	88.97 t	52.88	71.16 t	54.82	71.26 t	56.16	64.91 t	54.93	57.23 t	55.12	68.55 t